Condensation trails from biofuels / kerosene blends scoping study

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Abstract

The purpose of this report is to inform the European Commission on issues related to contrail formation with respect to the introduction of biofuels and blends (and similar alternative fuels) into the aviation transport system. The report describes the physics of contrail formation and how exhaust soot and other particles may affect contrail properties and eventual climate impact. Soot and particle formation depend on fuel composition and on details of the combustion process and the engine's influence on the latter. All these processes are discussed. Current uncertainties are stressed and ways to overcome them are suggested. The introduction of aviation biofuels has a potential for a climate benefit in principle, but further research is recommended in order to employ constrained stocks of biofuels in a climate optimal way.

Executive Summary

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Contrail formation is affected by two fuel properties, the emission index of water vapour (i.e. the mass of water vapour that is emitted from an engine when one kilogram of fuel is burnt) and the lower heating value of the fuel. A transition to alternative fuels[1] will lead to minor changes of these properties, consequently to minor changes of contrail formation conditions. In particular, contrails from alternative fuels will typically form at a slightly higher ambient temperature (ca. 0.75°C) than contrails from kerosene. Since temperature decreases upwards in the troposphere, on average with a rate of 0.65°C per 100 m, contrail formation will begin at about 100 m lower altitude in cases when a neat alternative fuel is burned instead of kerosene. These moderate changes will be proportionally smaller when instead of neat fuels blends are used. Further away from the contrail formation threshold, that is, at higher flight levels and lower temperatures, contrails form anyway independent of fuel type. Thus, a transition to alternative fuels will affect contrail formation only at the formation threshold, not at higher cruise levels. Statistics are lacking of how often flights occur at or off the threshold.

Measurements show that burning of alternative fuels and blends leads to a substantial reduction of soot emissions (by mass and number), mostly attributed to the reduced presence of aromatics when compared to Jet A-1. This in turn will lead to a reduction of the initial ice crystal number concentration of contrails from such alternative fuels under a wide range of conditions. Reduction of the initial ice crystal concentration has a strong potential for climate benefits if the reduction factor exceeds 5 or so (i.e. minus 80%); small reductions have a minor effect. The climate benefits are caused because crystals from biofuels are less in number, but larger than crystals from kerosene under equal ambient conditions. This leads to smaller optical thickness, lower radiative forcing, and lower lifetimes of contrails from biofuels compared to contrails from standard kerosene. Note however, that too strong reduction of soot (by a factor of 1000 or so, which might be achievable by a combination of lean combustion and alternative fuels) allows volatile and ambient particles taking over contrail ice

[1] The term "alternative fuels" includes fuels that are similar to kerosene, like drop-in fuels, but not liquid hydrogen or methane.

formation, which may overcompensate for the ice reduction due to soot reduction at very low temperatures.

The contrail-related climate benefit of an introduction of biofuels depends strongly on the particular meteorological situation; two contrails produced from the same fuel and the same aircraft/engine combination, but in different environment, may differ by more than two contrails from different fuels produced in the same environment. Climate benefit of biofuels will thus be larger or smaller depending on the particular situation. It may be larger in certain regions and certain seasons than in other regions and seasons. As stocks of biofuels will probably not suffice to supply the whole fleet, biofuels should primarily be employed when and where they produce the largest benefit for climate. More research is needed to find out under which circumstances a large benefit accrues.

Emission prediction models are required to analyse the impact of alternative fuels on engine emissions, particularly in terms of PM. It is suggested, that simple emission models should focus on both, characteristic engine performance parameters and fuel characteristics for the correlation with PM emissions, since the PM emission changes with engine power setting and fuel composition. However, a sufficient experimental database is essential.

The formation of emissions, in particular of soot particles, is considered to have the potential of a noticeable impact on climate. The formation of soot particles is resulting from the specific components of the fuel of interest. Soot formation is mainly due to fuel aromatics, but not all types of aromatics have the same soot formation potential. As 8 vol% aromatics must be in any fuel, according to the aviation jet fuel's specification, it is worth to investigate by a combined experimental and modelling effort, including lab, ground and flight tests, the role of different aromatics for soot and ice crystal formation, respectively. Similarly, the role and amount of cyclic and long-chained paraffins needs to be clarified.

Such measurements are difficult and corresponding data sparse due to the complexities in a jet fuel in conjunction with the wide parameter range when burning in a jet engine, under turbulent conditions and at high altitude. Potentially each process occurring in a combustion chamber, whether it is related to the fuel placement, to the ignition, to the split between the pilot burner and the main burner, to the staging, to the cooling, to the dilution, etc., has an impact on emissions. Furthermore, instrumental uncertainties need to be better quantified. Novel low-soot engines (lean combustion) should be tested as well, on existing and future engine architectures and combustion system technologies, ideally in combination with alternative fuel and kerosene. This would allow measuring a maximum possible range of soot emission and its effect on contrail formation and properties.

To be able to study the impact of fuel's composition on individual sub-processes, the recommendation is to study all of these sub- processes isolated in existing or to-be-designed specific experiments and rigs. Then, the proper metrology and diagnostics coupled with research simulation codes can give access to qualitative knowledge and quantitative measurements which allow understanding the true relationship between fuel composition and the sub-process under investigation. Moreover, following this strategy, will offer the possibility to study the combustion behaviour of future aviation fuels.

Furthermore, the need of developing validated chemical models is stressed. Such a model will allow studying the effect of the chemical composition of the fuel of interest on the fuel's properties, in particular on the combustion process, i.e. its emissions, and thus, the evaluation of its impact on climate. Thus, it is ensured that the combustion process and the emission pattern can be studied in detail, for a specific question, e.g. effect of a specific aromatic molecule or on other molecules, e.g. cyclic

or iso-alkanes on the amount of soot particles, within the whole parameter range. This was identified as a major open question.

Of course, the reaction model has to be validated against the relevant parameters and fuels, with representative molecules for the chemical families an alternative fuel might be composed of, and model fuels mimicking a synthetic fuel, among them.

In addition, once a reaction model exists that was validated by measurements covering the whole range of experimental parameters needed, CFD simulations can be used to predict the emission pattern of the fuel of interest under real flight conditions, i.e. taken into account the interactions between fuel placement, fuel combustion, and turbulence imaging the oxidation of a jet fuel in a jet turbine.

As it will probably take some decades to introduce novel fuels and combustion concepts comprehensively in the world aviation fleet, it is necessary to simultaneously develop mitigation options that will be ripe in a nearer future. A more climate-friendly aviation system can be achieved when climate impacts from individual flight's emissions are calculated already in the flight planning phase. This information can be used for routing, when a balance between climate costs and the traditional airline costs is seeked. Persistent contrails can be avoided when flights in ice-supersaturated regions are avoided. It suffices, however, to avoid those contrails that would produce the strongest warming effect, which requires that regions and times where contrails would strongly warm can be reliably predicted in advance of the flight. Methods for such predictions are in principle available, but still need operational tests and demonstration studies.

0. Introduction

The European Union is promoting the use of renewable energy in transport with an objective of 10% renewable energy in transport by 2020 as set out by the Renewable Energy Directive[2]. The use of biofuels is one way of meeting these targets. In this context, the Biofuels FlightPath is a private-public initiative amongst the EU aviation sector, leading companies developing technologies for advanced and sustainable biofuels and the European Commission. This initiative was launched in 2011 with the primary aim to mobilise all stakeholders ensuring that 2 million tons of sustainable biofuels are used annually by the aviation sector by 2020. This industry wide initiative aims to speed up the commercialisation of aviation biofuels in Europe.

There are specific environmental issues in aviation due to particulate emission, condensation trails, NO_X (nitrogen oxides) and ultrafine particles. These issues might be aggravated or mitigated in a transition to biofuels, thus requiring further studies. In this report we present a study on the effect of biofuels in the formation of contrails. The study covers the whole process chain from fuel placement and combustion via engine performance and emission formation to contrail formation and climate impact.

Contrails form when the so-called Schmidt-Appleman criterion (Schmidt 1941, Appleman 1953; see Schumann 1996 for a modern derivation) is fulfilled. The Schmidt-Appleman criterion can be derived from physical principles of mass, momentum, and energy conservation, that is, it is based on principles of dynamics and thermodynamics. It states that a contrail is formed once the mixture of exhaust gases and the ambient air becomes transiently (super-) saturated with respect to liquid super-cooled water. Contrails are of relevance for climate change only when they are persistent which requires their formation in an environment where the water vapour is (super-) saturated with respect to ice, so-called ice supersaturated regions (ISSRs). The general properties of ice supersaturation and the climatology of these regions are described by Gierens et al., 2012.

The Schmidt-Appleman criterion is valid for all types of fuels, kerosene, liquid hydrogen, and methane, alternative fuels derived from the Fischer-Tropsch process using coal-to-liquid, gas-to-liquid, and biomass-to-liquid, and biofuel from hydroprocessing (as HEFA). The criterion depends on atmospheric parameters (pressure), aircraft parameters (overall propulsion efficiency), and fuel parameters (the energy specific emission index of water vapour, that is, the ratio between the emission index of water vapour, EI_{H2O}, and the lower heating value of the fuel, LHV). EI_{H2O}/LHV of hydrogen and methane are much larger than that of kerosene, thus allowing contrail formation in warmer layers (i.e. lower flight levels) of the atmosphere than kerosene. Hydrogen and methane are not further considered in this study which concentrates on “drop-in” fuels, i.e. fuels that can be used in available engines and stored and transported to airports with current infrastructure. Drop-in fuels have EI_{H2O}/LHV similar to that of kerosene. Thus we expect that contrail formation itself from kerosene and drop-in fuels is not very different. However, contrail properties (i.e. ice crystal number concentration, ice mass, crystal size, and derived quantities) can be very different because drop-in fuels lead to particulate emissions that can be quite different from that of kerosene, and these particles serve as nucleation centres for ice crystal formation. The study will thus concentrate on the particulate emissions of various fuels and their effect on contrail properties.

[2] Directive 2009/28/EC of the European Parliament and of the Council of 23/04/2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC

Climate impacts will be expressed in terms of radiative forcing (RF, units W/m²). This and further metrics are described in various IPCC reports and in Fuglestvedt et al., 2010. We will not use other metrics like global warming potential (GWP) and global temperature potential (GTP) as (1) their calculation is based on RF anyway, (2) needs the subjective value-laden specification of a time horizon, and (3) depends on a so far unknown efficacy value for contrails cirrus. The efficacy of linear (young) contrails is probably smaller than one; but there are currently only two inconsistent estimates, 0.6 and 0.3 (Ponater et al. 2005; Rap et al. 2010). The efficacy value of contrail-cirrus (old broadened contrails that visually look like natural cirrus) is not known at all.

1. Literature study

1.1. Contrail formation: influence of fuel type

Although the Schmidt-Appleman criterion does not mention particles at all, contrail formation would not be possible without particles which serve as nucleation centres for the formation of liquid droplets and ice crystals. It is not necessary that the formation criterion mentions particles because they are always present in the exhaust gas in large numbers. Even if the exhaust is free of particles as in the case of liquid hydrogen (LH2) based propulsion, there are still sufficient numbers of particles in the ambient air that serve as nucleation centres, such that even cryoplanes (those propelled with LH2) would produce contrails (Ström and Gierens 2002). Particulate emissions from different fuels differ and this has immediate consequences for contrail properties and indirect consequences for their climate impact. Thus it is necessary to review first the knowledge on particulate emission from fuels, kerosene and alternatives.

1.2. Particulate emissions from kerosene and alternative fuels

1.2.1. Kerosene

Kerosene is essentially a mixture of hydrocarbon chain molecules with a predominant fraction of straight and branched alkanes, C_nH_{2n+2}, with typically $8 \leq n \leq 16$ (Blakey et al., 2011). Cycloalkanes are present as well. They help to keep the fuel freeze point low, an essential property for flying in high altitudes. Kerosene contains aromatics (up to 25% by volume) which are precursors for soot. Further trace species are present in kerosene, from which we only consider sulphur because of its role in formation of volatile particles in the exhaust.

As a result of incomplete combustion of the hydrocarbons, aircraft engines emit black and organic carbon (BC and OC), which both contribute in different shares (depending in particular on power setting) to soot particles[3]. The BC fraction of total carbon (TC) emitted increases strongly with power setting at low powers, and stays approximately constant (approx. 0.7 to 0.8 of TC) at power settings above 50% (Petzold et al., 1999, similar results from APEX and AAFEX). The OC fraction of TC depends on the exhaust gas temperature, and thus on combustor temperature and air-fuel ratio. Higher temperature leads to a more complete combustion, hence a lower OC/TC. Aircraft combustor soot consists of primary spherical particles with diameters in the range of a few tens of nm, which quickly form larger fractal aggregates of 100 to 500 nm size in the exhaust plume. The PartEmis[4] experiments have shown that properties of the emitted soot, at engine exit, are almost completely determined by the combustor while the turbine section of an engine has no significant influence (Petzold et al. 2005). Measured BC mass emission indices, EI_{BC}, are of the order 10^{-5} kg BC per kg fuel burnt at idle to $10^{-3.5}$ kg/kg in cruise, where values measured at ground tests (cruise thrust) seem to be higher than corresponding values in flight. BC number emission indices are 10^{14} to 10^{15} per kg fuel in ground tests and about double this value (1.75×10^{15} kg^{-1}) in flight tests (Petzold et al., 1999). Soot mass and particle

[3] Black carbon consists of pure carbon in unspecified form, e.g. as graphite. It is responsible for the black colour of soot (i.e. it strongly absorbs light). In contrast, organic carbon absorbs weakly in the visible spectral region.

[4] The PartEmis (Measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines) project was funded by the European Commission and by the Swiss Bundesamt für Bildung und Wissenschaft under contracts no. G4RD-CT-2000-00207 and 99.0632, respectively.

emission indices are of the same order of magnitude as BC, with corresponding fleet averages computed for 1992 of 0.04 g/kg and 1.2×10^{15} kg^{-1}, respectively.

Aircraft engines emit charged molecular clusters, so–called chemi-ions, with an emission index of the order 10^{17} per kg fuel (Arnold et al., 2000). These are positively and negatively charged particles of few nm size with concentration at engine exit, measured at ground, of about 10^9 cm^{-3}. Mutual coagulation, recombination and condensation of chemi-ions on other particles in the plume quickly lead to a reduction of their number density. Negatively charged ions contain sulphate and sulphuric acid compounds as well as organic ones, while positive ions consist of oxygen-containing organics. These ions are important for formation of volatile aerosol particles.

The emission index of volatile particles[5] with diameters larger than 1.5 nm is about 2×10^{17} kg^{-1}, similar to the number of chemi-ions, which promote their formation. Obviously much more (100 to 1000 times) volatile than soot particles are present in the exhaust, but when a contrail is formed more than 75% of the volatile particles can be scavenged by the ice crystals. Volatile particles consist mainly of sulphuric acid (in particular at high fuel sulphur content) and condensable organic matter.

Kerosene contains sulphur in an average proportion of 400 ppmm (mg per kg fuel, usual values range from 10 to 1000 ppmm, and the specification limit is 3000 ppmm). Burning kerosene produces SO_2 with an emission index of about 0.8 (0.6–1.0) g kg^{-1}, or 800 ppmm as expected for a complete combustion of the sulphur (the molecular mass of SO_2 is double that of elementary S). A few percent of the SO_2 is further oxidized into SO_3 which reacts with water vapour to form H_2SO_4 (gaseous sulphuric acid). The emission index of H_2SO_4 is about 0.04 g kg^{-1} (0.01 to 0.1). This gas has an extremely low saturation vapour pressure and therefore readily condenses together with water vapour into aqueous solution droplets of sulphuric acid, after sufficient dilution and cooling of the exhaust gas (Vancassel et al. 2004). Accordingly, fuel sulphur is an important source of volatile particles in the exhaust. However, the number concentration of volatile particles is only a very weak function of the fuel sulphur content. A flight experiment with the DLR ATTAS consuming fuels of different sulphur contents in its two engines, 6 and 2700 ppmm, showed that the number of particles in the 10 s old plume increased by a factor of 3 to 4 from the low to high sulphur exhaust plume (Petzold et al. 1997), while the ratio of the fuel sulphur contents was 450 (see also Schumann et al. 2002, Fig. 7). Thus there must be sink processes acting in the plume leading to a strong buffering effect in the relation between sulphur content and concentration of volatile particles including droplets of sulphuric acid solution. Indeed, the sulphuric acid droplets and condensable hydrocarbons condense together with water vapour on soot particles, thereby enhancing the ability of the latter to serve as condensation nuclei for contrail formation. Also later sulphuric acid solution droplets can coagulate with remaining soot and ice particles.

In ground tests (AAFEX, Beyersdorf et al. 2014), emission of volatile particles decreased with increasing power setting by a factor of about 3 between idle and full power, mainly because unburned hydrocarbons get reduced with increasing power. The formation of volatile particles depends on ambient temperature and increases with decreasing temperature, by about a factor of two between 20°C and 0°C.

The condensation of H_2SO_4 and other soluble compounds like soluble OC on soot leads to a so-called coating. The coating typically consists of up to a few percent by volume. Its thickness expressed as number of monolayers[6] depends on the fuel sulphur

[5] In contrast to combustion particles like soot which are thermally stable up to temperatures far above 400 K, volatile particles sublimate at about 400 K.

[6] A monolayer is a single layer of molecules on the surface of a substrate.

content and the size of the soot particles; it does not exceed a few monolayers. Coating of soot particles with water soluble matter enhances their ability to form droplets by spontaneous water condensation; coating with insoluble OC decreases it. Once droplets are formed they freeze quickly resulting in contrail ice crystals. The fraction of soot particles that lead to droplets and ice crystals depends mainly and strongly on the maximum transient supersaturation (with respect to water, $S_{w,max}$) achieved in the expanding and cooling exhaust plume. The fuel sulphur content plays a relatively large role under threshold conditions (i.e. low $S_{w,max}$). For instance, 100 nm spherical insoluble soot cores (0 and 3 vol % coating) have activation fractions of 3×10^{-4} and 0.02 at 1% water supersaturation, but already 0.25 and 0.53 at 5% supersaturation. Essentially all soot cores later form an ice crystal at even higher supersaturation. The Schmidt-Appleman criterion is just fulfilled when 1 and 5% supersaturation is reached in the expanding plume (that is, these can be considered threshold conditions).

Much more details on these emissions, their sensitivity to many parameters, how they have been measured, etc. can be found in Schumann et al. (2002).

1.2.2. Drop-in fuels

The definition of Drop-in fuels used in the present report stems from the SWAFEA Study (2011). From the most general point of view, a "drop-in" fuel is a substitute for conventional jet fuel, which is fully compatible and interchangeable with conventional jet fuel. Such an alternative fuel doesn't require any adaptation of the aircraft and of the infrastructure, and doesn't imply any restriction on the domain of use of the aircraft. It can be used just as conventional jet fuel and doesn't require any new certification of the systems. The "drop-in" property is today seen as a major requirement for any new fuel in aviation and has been the target of the development and approval of the first alternative fuels in aviation. For example, the 100% SPK fuels used during the AAFEX ground measurements are not drop-in fuels.

Such alternative drop-in fuels can be derived from bio-renewable resources (plants, algae, animal fat) and from fossil resources, coal or natural gas. While essential fuel properties of these alternatives are similar to kerosene, e.g. density, viscosity, lower calorific value, ignitability and re-ignitability, their chemical composition is different from petroleum-derived kerosene. The Fischer-Tropsch process converts so-called syngas (a mixture of H_2 and CO derived from the mentioned feedstock) into a fuel primarily composed of hydrocarbon molecules (in the AAFEX experiments they were alkanes with $8\leq n\leq12$, that is, shorter chains than in kerosene; Moore et al. 2015), with very little aromatics and no sulphur. The low aromatic content generally leads to reduced soot production and the lack of sulphur implies that no sulphuric acid is produced in an aircraft plume, hence no volatile aerosol consisting of aqueous solutions of sulphuric acid. Nevertheless, sulphuric acid solution droplets are present in the background atmosphere and can be entrained into the plumes. A simple estimate, assuming a background concentration of sulphuric acid of 10^{-13} g/cm^3, a typical fuel flow of 10 g/m and an average H_2SO_4 emission index of 0.04 g/kg for kerosene, shows that the contributions from kerosene combustion and ambient air to the plume's acid concentration are about equal when the plume diameter is about 70 m, which is achieved in less than 0.5 s. This result implies that the only effect of no sulphur in the fuel on contrail formation can be that the soot particles have not yet a sulphuric acid coating at engine exit but they will acquire a coating soon. Thus contrail formation cannot be avoided by using sulphur-free fuel; it can only be delayed, which may result in different microphysical and optical properties.

1.2.3. Comparison between particulate emissions from drop-in fuels, blends, and kerosene

Biofuels and FT fuels are very poor in aromatic content. This causes problems with seal shrinking and thus aromatics must be added to drop-in fuels in flight tests such that a concentration of 8% is achieved (Blakey et al. 2011). Novel seal materials will probably overcome this problem in future. The low aromatic content leads to a low tendency of the alternative fuels to form soot since soot formation proceeds from polycyclic aromatic hydrocarbons (PAHs, in particular naphthalene) via hydrogen abstraction and carbon addition (the so called HACA process). If aromatics are low, soot formation requires as a first step the initial formation of aromatic rings before HACA can proceed. Thus, fuels with low aromatics content have lower soot emissions than kerosene. It seems that PAHs are easier formed from branched than from straight alkanes. Alternative fuels with branched alkanes have thus a higher sooting tendency than fuels with straight alkanes (DeWitt et al., 2008), but still on a comparatively low level. During AAFEX (Alternative Aviation Fuel Experiment), two neat FT fuels were used, a CtL one, predominantly consisting of branched alkanes (i-alkanes), and a GtL one, consisting mainly of straight alkanes (n-alkanes). The CtL fuel had higher soot emissions than the GtL fuel, probably due to the differences in the predominant alkanes (Beyersdorf et al., 2014).

Unexpectedly, constituents like sulphur and aromatics can be enriched or depleted in blends. Usually one would expect in a 50/50 blend (equal volumes) to find a sulphur content that is the density weighted arithmetic mean of the sulphur contents of the original fuels (in ppm by mass), i.e.

$$\rho_{Blend}[S_{Blend}] = ½ \, (\rho_{Kerosene}[S_{Kerosene}] + \rho_{alt}[S_{alt}])$$

(where ρ_X is the density (kg m^{-3}) and $[S_X]$ is the sulphur concentration by mass (ppmm or mg per kg) of fuel type X) but this is not found. In the AAFEX experiment, the density weighted arithmetic mean of the sulphur contents of JP-8 and FT1 is 612 ppmm, but the blend has a sulphur content of 699 ppmm, 87 ppmm more than the arithmetic mean (or 14% of 612 ppmm). All quoted values are reported in table 2 of the AAFEX report (Anderson et al. 2011).

Surprisingly, for the aromatics we have 14% too little in the blend. As the concentration of aromatics is given in volume percent (vol%), we can use the arithmetic means of the concentrations given in the tables. We expect to find in Blend 1 of AAFEX an aromatic content of 9.3 vol%, but measured is 8 vol% which is only 0.86 from 9.3%, i.e. 14% too little. From this, it seems that simple explanations with inexact mixing and remaining kerosene in the pumps and tubes sound implausible. Other explanations are currently not available (Dr. Moore, NASA, private communication). These implausible results are contrarious to statements in the HBBA interim report, where it is said that volume or mass related parameters like sulphur content mix linearly in blends.[7] Other parameters, like freezing point, are not expected to behave linearly with blending, and indeed they display a more complex dependence on blend ratio. Emission indices belong to the latter group of parameters.

The problem just mentioned and others make the experimental determination of emission indices for alternative fuels difficult and prone to large uncertainties. It is however much easier to determine ratios of emission indices, if, as usual, in experiments one engine is running on kerosene while the other is running on a neat alternative fuel or a blend. If measurement errors are the same for both types of fuel, which can reasonably be assumed, these errors cancel by taking ratios. Taking ratios also reduces the variation over the full range of powers. In this way it was found in

[7] HBBA (High Biofuel Blends in Aviation, ENER/C2/2012/420-1) interim report, section 1.3

AAFEX that $EI_{BC}(FT)/EI_{BC}(JP\text{-}8)\approx 0.14\pm 0.05$ and $EI_{BC}(Blend)/EI_{BC}(JP\text{-}8)\approx 0.34\pm 0.15$. These are strong reductions, but still stronger reductions were obtained for number emission indices, in particular at medium power: $EI_{soot,N}(FT)/EI_{soot,N}(JP\text{-}8)\approx 0.05$ and $EI_{soot,N}(Blend)/EI_{soot,N}(JP\text{-}8)\approx 0.15$ (Beyersdorf et al., 2014). It is evident from these results that reductions are stronger than proportional to the share of alternative fuel in the blend, probably a consequence of the fact that soot formation needs the reaction of certain components in the fuel that are only present in kerosene (e.g. the aromatics). Let their concentration be [A]; then their reaction rate is proportional to $[A]^2$, which shows that in a 50% blend $[A]^2$ is reduced by 75% relative to 100% kerosene. In view of this simple reaction-kinetics consideration, disproportionately high soot reductions are no surprise. However, Beyersdorf et al. write that soot production is proportional to aromatic content (and inversely proportional to hydrogen content), a statement that seems neither to be supported by these results nor by theoretical expectations. Earlier experiments (Timko et al. 2010, and Lobo et al. 2011) resulted in similar reductions of emission index ratios at idle power, but in significantly smaller reductions at 85% power. Timko et al. (2010) even found no reduction in neither EI_{BC} nor $EI_{soot,N}$ at 85% power for blended fuels. This shows that still large uncertainties prevail in such measurements. Statements of proportionality between blend ratios (aromatic content) and soot reductions should currently not be taken too seriously.

As with kerosene, soot emission (by mass and number) from alternative fuels depends on power setting. EI_{BC} increases as function of F/F_0, in particular for $F/F_0>45\%$. $EI_{soot,N}$ has a minimum at 45% thrust and is higher at idle and at full power (Beyersdorf et al., 2014). The following explanation is offered for these dependencies: The higher F/F_0, the more primary soot spherules are produced and emitted. Coagulation of these leads to larger but less soot particles as long as F/F0 <45%, but if power is further increased, the rate at which new primary particles are produced exceeds the rate at which they coagulate to form aggregates; hence the concentration of particles rises again. If this interpretation is correct, one should find predominantly primary spherules at low power, primarily aggregates around 45% power, and both soot aggregates and primary soot spherules at high power settings. Volume mean diameters of soot particles are largest for kerosene, smallest for neat FT, and intermediate for the blends for all power settings. Accordingly, the effective density of these particles (mass per volume) behave in the reversed order, that is, $\rho(FT)>\rho(blend)>\rho(kerosene)$.

Although details are different between various measurement campaigns, all agree on the following points: emission indices of soot (mass and number related) are highest for pure kerosene, lowest for pure FT fuels, and intermediate for blends, as expected from the considerations above. Largest soot reductions are given for low engine thrust (idle) and the reductions decrease with increasing thrust (Beyersdorf et al., 2014).

Formation of volatile particles in the expanding and cooling exhaust plume (based on emissions of sulphur dioxide and unburned hydrocarbons, UHCs) from alternative fuels is reduced compared to kerosene. Evidently, SO_2 emissions are strongly reduced because of very low or even absent sulphur in FT fuels. Correspondingly, a very strong reduction of 94% of the number-based emission index for (all, i.e. volatile and non-volatile) particles has been measured 30 m behind the engine exit plane when neat FT fuel was burned, similar to the reduction at exit plane (where only non-volatile soot particles can exist). However, the reductions were smaller for blends (30-44%) at 30 m distance than at engine exit (64%, Beyersdorf et al. 2014). Timko et al. (2010) found similar results and explained them with the influence of soot surfaces which can scavenge the volatile particles.

The results reported above have all been obtained in ground based experiments (APEX, AAFEX). Meanwhile, two airborne campaigns have been conducted (ACCESS I

and II); preliminary results of these campaigns have been reported on workshops, but are not yet publically available.

1.3. Physico-chemical properties of combustor soot

1.3.1. Structure and composition of combustor soot

It is well known that pure graphite is hydrophobic, that is, there is hardly any water adsorption on graphite even when the relative humidity is near 100%. Thus it was hypothesised that (at least partial) sulphuric acid coating on soot surfaces is needed to form contrails. However, contrails form even when the fuel is almost free of sulphur, thus the question arises about special properties of jet engine combustion soot that makes water adsorption possible, at least at 100% relative humidity.

Soot properties depend strongly on the formation process, that is, spark generator soot, lamp soot, burner soot, etc. differ in certain qualities from jet engine combustor soot. Laboratory studies therefore need a gas turbine combustor to produce typical aircraft soot. Fuel composition and details of the combustion process have important impact on soot properties as well.

Popovicheva et al. (2004) and Demirdjian et al. (2007) studied gas turbine engine combustor generated soot in the laboratory with many techniques. For their experiments they burned TC1 kerosene[8] with fuel sulphur content of about 1100 mg/kg in a D30-KU engine[9]. The soot particles of this engine were collected 12 cm after engine exit on a cooled copper plate and later analysed. It cannot be excluded that this type of sampling leads to morphological modification of the originally emitted soot particles. The sampled soot consists mainly of agglomerates of roughly spherical primary particles. The sizes of the primary soot particles are 30-50 nm, similar to results from other measurements of aircraft soot, but there are larger particles of 100 nm as well. Most of these primary particles are amorphous with a relatively high density (0.4 g/cm^3) and a low specific surface area (9-30 m^2/g), compared to other forms of soot. The amorphous structure is typical for soot from diffusion flames. There are other soot particles having an onion-shell structure composed of nearly concentric graphene layers. This type of soot is typical for premixed flames. Additionally there are well-crystallised graphite flakes. These soot particles consist to 98 wt% of carbon; the rest is mainly oxygen (1-2 wt%) and sulphur (0.2 wt%). Although the sulphur content is small, it is higher than in the fuel. Simply burning TC1 kerosene in a wick lamp gives soot with sulphur contents below the detection limit. This shows that the combustion conditions in a jet engine probably lead to an accumulation of sulphur in the soot. Some of the combustion soot particles contain iron (up to 5 wt%).

A small fraction of the sampled soot particles is characterised by non-spherical shape, wide variability in size (4 nm to >100 nm), and a composition significantly differing from the spherical soot particles and graphite flakes. They contain a large fraction of various impurities, metals (in particular iron), oxygen and sulphur. The carbon content of the particles with impurities can be lower than 50 wt%; iron can make up more than 40 wt%, oxygen 10 wt%. It is remarkable, that these “impure” soot particles contain much more sulphur (2 wt%) than the “pure” soot particles mentioned above (0.2 wt%), perhaps triggered by heterogeneous reactions between iron and sulphur components.

[8] TC1 seems to be kyrillic. In another paper this kerosene was labelled TS1.
[9] Russian Tu-134 aircraft have this kind of engines.

It is quite possible that the fraction of impurities is a peculiar result of this experiment, due to abrasion from parts of the engine[10]. However, metallic particles in engine exhaust have been found in contrails as well (Petzold et al. 1998). Petzold et al. collected ice crystals, evaporated the ice and studied the residual particles (on which the water originally had condensed). They found that particles with diameters less than 0.5 µm are almost pure BC, whereas particles larger than 1 µm are either soot agglomerates or mixed particles with metallic inclusions. These are about 1% of the residual particles. Since both the almost pure BC soot particles and the particles with metallic inclusions are found in ice crystals, it is both groups that serve as condensation nuclei.

Jet engine combustor soot has a high content of water soluble material, about 13.5 wt% in the mentioned experiments, consisting of sulphates SO_4^{2-} (3.5 wt%), organic and inorganic ions, and other compounds. It is noteworthy that the water soluble substances are not dominated by sulphur components, which implies that sulphur-free fuel can produce soot with a substantial amount of water soluble material as well. These substances and active sites on the soot surface distinguish the soot's aptitude as condensation nuclei.

1.3.2. Hygroscopic properties and water adsorption

Water adsorption on soot surfaces is initiated by attachment (bonding) of water molecule's hydrogen ends to active sites on the surface of soot particles. These active sites are formed by certain chemical features, so-called functional groups, which have polar character. For instance there are carbonyl, carboxyl, and phenol groups, all involving either an oxygen atom or an OH group which both provide the possibility for polar binding of water molecules due to their own polar properties. Since these groups are already present 12 cm after engine exit, there was not enough time to condense on the soot surface between engine exit and the collector surface. The functional groups must accumulate on the soot already within the engine. On increasing the relative humidity, more water molecules cluster around the already bonded ones and at even higher RH capillary condensation in pores occurs. How much water is adsorbed seems to be quite variable from experiment to experiment. At water saturation, soot derived from burning TC1 in a wick lamp obtains the equivalent of a few (say 2-5, compare Demirdjian et al. 2007 and Popovicheva et al. 2008, working with soot from the same source) monolayers of water. The expression "equivalent monolayer" does not mean that the surface is actually covered completely with a water film; instead the water clusters around the active sites. The TC1 lamp soot was assumed to be a surrogate for the pure fraction of jet engine combustor soot in these experiments.

Polar functional groups on the "impure" soot fraction contain organic and ionic sulphates and carbonyl groups. These initiate water adsorption as in the pure soot fraction. However, once a water cluster around an active site comes into contact with water soluble substances, a liquid solution is formed covering a much larger surface than the clusters around the active sites would do alone. Water vapour can then be absorbed into the liquid solutions, which leads to much higher levels of condensation than adsorption alone. The large amount of water soluble substances on the impure soot particles lead to high levels of water content already at relatively high temperatures (295 K) and at low relative humidity (RH): A complete H_2O monolayer is already achieved at RH≈1%. About 20 monolayers are reached at 240 K and water saturation (Demirdjian et al. 2007). Again, a large variability of these values is evident from even much higher water contents found for the same kind of soot in further studies by essentially the same group of researchers (Popovicheva et al. 2008).

[10] The iron fuel atomiser is a good candidate. In an earlier experiment with the same engine but without the atomiser no iron was found in the soot.

It is not clear from these studies whether the impure soot fraction is actually needed for contrail formation, although it certainly helps. It is neither clear whether an impurity fraction is always present nor how large this fraction is on average or for certain engines (considering age, maintenance, wearing). Furthermore the amount of water soluble substances at the surfaces of the pure soot particles is unknown. The TC1 lamp soot, taken as a surrogate for the pure jet engine soot because of structural similaritiy, contains about 1 wt% of water soluble substances, but it is hard to explain how the engine soot (containing a pure main fraction and an impure trace fraction) can obtain 13.5 wt% of water soluble substances if the main fraction would only have 1 wt%. Thus it might well be that the pure engine soot contains more water soluble material than the TC1 lamp soot.

Anyway, it is probable that the pure combustor soot fraction suffices for contrail formation in cases where the Schmidt-Appleman threshold is safely exceeded (i.e. where the transient maximum water supersaturation attained in the expanding plume exceeds a few percent). Otherwise it is hard to explain why the Schmidt-Appleman criterion is so reliable. Only close to the threshold, if the pure soot does not adsorb much water (i.e. if there is indeed little water soluble material), the impure fraction can be expected to significantly contribute to droplet and ice crystal formation.

These laboratory experiments show that water condensation on jet engine combustor soot is initiated by adsorption at functional groups and can be significantly enhanced by absorption of water molecules into aqueous solutions forming from water soluble substances on soot. The functional groups are mainly characterised by polarity provided from oxygen atoms and OH, sulphur seems not to be necessary for this. Thus contrails can form even when sulphur-free fuel is burned. Sulphur is however accumulated in the impure soot particles where it contributes to the water soluble substances without dominating them. Sulphur-rich fuel can thus lead to a slightly earlier onset of contrail formation compared to a sulphur-poor fuel (Busen and Schumann 1995) because the impure soot fraction supports water condensation already before water saturation is achieved in the plume, but this effect is only relevant under threshold conditions.

1.4. Impact of gaseous and particle emissions on contrail properties

1.4.1. Contrail formation

Kärcher and Yu (2009) investigated how variations of aircraft soot emissions over a few orders of magnitude affect ice (i.e. contrails) formation in an aircraft exhaust plume. Since such an investigation is not possible experimentally, they used a parcel model that simulates the evolution of plume aerosol particles and ice microphysics, accounting for electrical charge effects (from chemi-ions) on liquid particle nucleation and growth. Entrainment of ambient particles is taken into account; these particles are assumed to consist of aqueous solution droplets of sulphuric acid with a concentration of 600 cm^{-3}. Thus, if soot activation needs the presence of sulphuric acid, this is always given in this study.

Simulations have been performed for three ambient conditions: temperature just at the Schmidt-Appleman threshold (223 K), and 5 and 10 K lower. The soot emission index by number, $EI_{soot,N}$, has been varied in the range (10^{12},10^{16}) per kg fuel and the number concentration of ice crystals formed after one second of plume evolution has been determined. Three regimes have been found, depending on the predominant ice formation agent. In the soot-rich regime, almost all ice crystals are formed by nucleation on activated soot particles. In the soot-poor regime, almost all ice crystals originate from homogeneous freezing of liquid droplets (without soot cores). Between these extremes there is an intermediate regime. Based on soot emission

measurements from ground tests (AAFEX), we can assume that the soot-poor regime is the relevant one for burning biofuels.

Conditions of $EI_{soot,N}>10^{15}$ per kg fuel lead to the soot-rich regime, see Figure 1-1. In this regime, the efficiency of H_2SO_4-coated soot particles to nucleate ice crystals is a very strong function of temperature. Between the temperature threshold and the 5 K lower temperature the fraction of soot nucleating ice increases from 9 to 98%, and all soot particles nucleate ice at the lowest considered temperature. Correspondingly, the ice number concentration after one second differs by a factor of about ten between the threshold temperature and the colder cases. The concentration of ice increases in power-law fashion with $EI_{soot,N}$ (i.e. $n_{ice} \propto (EI_{soot,N})^{\alpha}$ where $\alpha \leq 1$) and the contribution of liquid droplets to ice formation is less than 10% in the soot-rich regime.

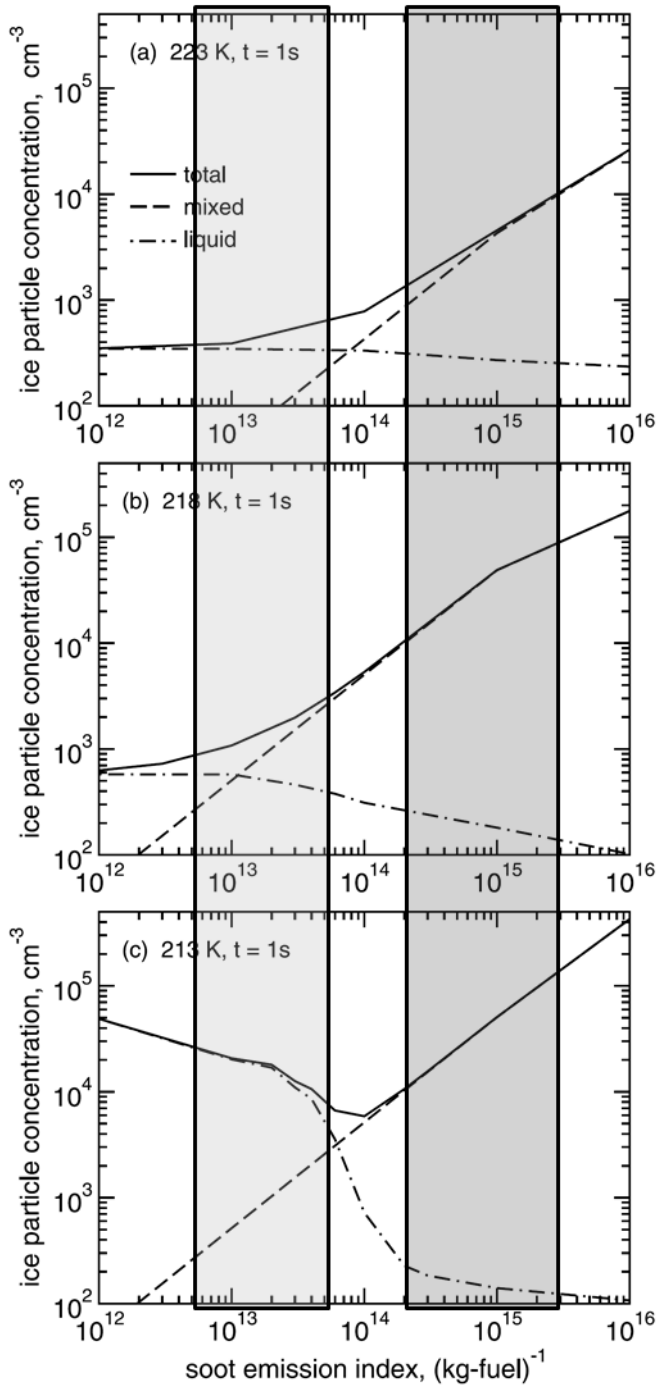


Figure 1-1: Concentration (cm^{-3}) of newly formed ice crystals in a contrail of 1 s age as a function of the soot emission index by number (soot particles per kg of fuel) from Kärcher and Yu (2009) with modifications. The dark grey box (right) represents a range of soot emission indices measured in the current fleet (Schumann et al. 2002), while the light grey box (left) represents probable emission indices for biofuels and blends. It has been placed using reduction factors reported from the AAFEX experiment.

The initial concentration of ice crystals is lowest a few degrees below the contrail formation threshold in the intermediate regime where the soot emission index is of the order 10^{13} to 10^{14} per kg fuel, that is, where per kg of fuel burnt about 10^{13} to 10^{14} ice crystals are formed. Typical ice crystal diameters are 2 to 3 µm.

The soot-poor regime, that is, where ice is formed predominantly by freezing of liquid droplets without soot cores, has $EI_{soot,N}<10^{13}$ per kg fuel at 223 and 213 K and even $EI_{soot,N}<10^{12}$ per kg fuel at 218 K. Freezing of the ambient solution droplets is predominant under threshold conditions. Liquid droplets from the exhaust only start contribute to ice formation a few degrees below the

threshold (because they are much smaller than the ambient particles), however their contribution increases strongly with decreasing temperature (by more than a factor 1000 with the 10 K considered). The resulting ice concentration even increases with decreasing soot concentration at low temperatures because the soot ceases to act as a sink for condensing water vapour, and this vapour is then available for growth of the droplets. This result shows that reducing soot emissions does not imply benefits for climate under all circumstances.

Rojo et al. (2015) used a trajectory box model with detailed aerosol microphysics to simulate the evolution of aerosol and ice in young (less than 10 s) exhaust plumes from aircraft engines driven by pure kerosene, pure alternative fuel (FT or HEFA), and a 50/50 blend of these. The microphysical model treats the following particle types: neutral and negative sulphate clusters, dry soot and activated soot (i.e. soot covered partly with hygroscopic material like sulphuric acid or condensable organics), neutral and positive organic clusters, mixed aerosol (neutral, negatively or positively charged), and finally ice crystals. For the latter, the model distinguishes between crystals formed homogeneously (i.e. by freezing of liquid aerosol droplets) and heterogeneously (ice formed on activated soot surfaces). The organics can be soluble and insoluble. The soluble ones can be collected by soot particles and the insoluble ones can adsorb on soot particles. Only the soluble fraction leads to activation of the soot. The soluble organic matter is present in higher quantities than the insoluble fraction. Going from pure kerosene to pure alternative fuel increases the ratio soluble/insoluble organic matter. With this model, the microphysical evolution of an exhaust plume is simulated for a certain temperature and relative humidity, that is approximately ice saturated and a few (2-3) K below the Schmidt-Appleman limit, that is, a condition that allows contrail formation. The model is run in two configurations, one without ambient aerosol and one with 500 cm^{-3} ambient soot particles (compared with average background concentrations in the upper troposphere of perhaps 30 cm^{-3} this assumption represents heavily polluted conditions which might obtain in a region with dense air traffic).

It turns out that ignoring the presence of ambient particles is justified both for kerosene and blend exhausts, but not for exhausts from pure alternative fuels. Pure kerosene and blends show quite similar temporal evolution of supersaturation in the plume. Transient small differences vanish almost completely after one second. Also the mean sizes of volatile particles, in-activated soot, and ice crystals develop quite similar in the first second. After 0.5 s, ice crystals in the blend plume are a bit larger (2 µm) than those in the kerosene plume (1.5 µm). The number concentrations differ by a factor of 2 (i.e. the kerosene contrail has twice the ice crystals than the blend contrail). This ratio is equal to the ratio of the assumed number concentrations of soot particles emitted from kerosene vs. blend burning engines, and this is expected for the soot rich regime a few degrees below the Schmidt-Appleman limit (cf. Kärcher and Yu, 2009). However, the number of non-activated soot particles after 0.5 s differs by a factor 20, and these particles differ also in their chemical composition.

For pure alternative fuel, the soot does not activate because of lack of sulphuric acid in the plume (this assumption is contrarious to the results mentioned above in section 1.3). However, assuming absence of ambient aerosol (or ignoring it), ice forms homogeneously on volatile particles. Ice formation is slightly retarded relative to the other cases and supersaturation lasts longer, giving the volatiles sufficient time to grow by condensation of water vapour and freeze. After 0.5 s the ice contrail is very similar to that of pure kerosene in terms of crystal number concentration, mean crystal size, and crystal size distribution. These results might change with different ambient conditions. If ambient soot particles are taken into account, results change quite substantially. In this case there are still many homogeneously formed ice crystals, but considerable less (perhaps 30%) than without ambient soot. Additionally

there is a small fraction of ice formed heterogeneously on ambient soot that has been activated by collecting condensable and soluble organics after entrainment into the exhaust plume. In spite of that, the total number concentration of ice crystals (homogeneously and heterogeneously formed) is much less than without ambient soot. Seemingly, the heterogeneously formed ice starts to grow, thus consuming the excess water vapour (vapour in excess of ice saturation). This process (as is known from cirrus formation, cf. Gierens 2003) can reduce homogeneous ice formation substantially.

It would be premature to base conclusions on these few simulations. More ambient conditions (temperature, humidity, aerosol concentration) must be considered before general tendencies could be deduced.

The assumption of the composition of ambient particles constitutes a major difference between these two studies, namely sulphuric acid solution droplets vs. soot particles. Under soot-rich combustion conditions, these differences have hardly an effect, but there may be effects under the conditions that interest when considering combustion of biofuels. It may be said here that while aqueous acid solution droplets are ubiquitous in the upper troposphere, a relatively high concentration of soot particles as assumed by Rojo et al. constitutes a heavily polluted air mass; such pollution can originate from dense air traffic and from industrial emissions transported into the upper troposphere by convection. In this sense, both studies are complementary. The results of Kärcher and Yu are valid for clean air masses only, while the typical background aerosol and its potential role for activating emitted and entrained soot is neglected by Rojo et al. and this might have an effect on their simulation of the pure alternative fuel. There are further differences between the two studies. Kärcher and Yu assume that contrails form mainly by homogeneous freezing of water-activated soot (RH_w>100%, that is, water-supersaturated conditions) and liquid (exhaust and ambient) droplets. Heterogeneous ice nucleation on soot may contribute, but as the relative humidity for this process must still be close to water saturation (otherwise disagreement with measurements occurs), the results are not significantly affected by that pathway. Rojo et al. model ice formation on soot as heterogeneous nucleation (at a critical relative humidity not mentioned in their paper, and only occurring in presence of sulphuric acid which sounds inconsistent with the assumption of heterogeneous ice nucleation), and reserve homogeneous nucleation for freezing of liquid solution droplets. This difference is probably uncritical to the further interpretation.

There is a small effect on contrail formation that originates from the fuels different hydrogen/carbon (H/C) ratios which are higher in alternative fuels than in kerosene. In the AAFEX experiment, one of the Fisher-Tropsch fuels had a 16% higher H/C ratio and a 14% higher H mass fraction than standard JP-8 kerosene, corresponding to a 14% higher emission index for water vapour, EI_{H2O}. The higher H fraction implies also a higher calorific value, LHV, of the alternative fuel, such that the so called energy specific emission index for water vapour, EI_{H2O}/LHV, of these alternative fuels may be 10% larger than that of kerosene. This leads to a higher threshold temperature at which contrails can form of about 1 K which in turn corresponds to a lower minimum altitude for contrail formation of 100 to 150 m.

1.4.2. Vortex phase sublimation of ice

The initial reduction of ice crystal number concentration when burning alternative fuels instead of kerosene will be damped by sublimation of ice crystals in the vortex phase. Airplane aerodynamics leads to a downward travelling pair of vortex tubes that last a couple of minutes until the vortices become instable and decay. The vortex pair travels downward with a speed of typically 2 m/s (depending on weight, span, and true air speed). Contrail ice crystals are caught within and transported downwards with the

tubes. Downward transport implies pressure increase, adiabatic rise of the temperature, and thus increase of the saturation vapour pressure, or equivalently, decrease of the relative humidity. Once the relative humidity (with respect to ice) gets below 100%, ice crystals start to sublimate, and the smallest ice crystals vanish the first. The overall crystal loss from the contrail during the vortex phase can range from nearly all to nearly nothing, depending on temperature and its variation with altitude near the contrail, ambient humidity, and the size distribution of ice crystals. Example results of this process can be found in Unterstraßer (2014). As a kerosene contrail has, on average, smaller ice crystals than a contrail from alternative fuels, a higher fraction of ice crystals sublimates from the kerosene contrail than from the alternative-fuel contrail. The climate impact of the eventual contrail cirrus depends predominantly on the crystal concentration after the vortex phase (and of course on the prevailing meteorological conditions). Thus the climate benefit of alternative fuels cannot be estimated solely from the reduction of the soot number emission index or the initial crystal concentration. The ice sublimation during the vortex phase has to be taken into account. Simon Unterstraßer (DLR-PA) has derived an empirical formula for the sublimation fraction. According to this formula, a reduction of the initial ice number concentration by a factor of 100 results only in a reduction factor of 40 at the end of the vortex phase (Unterstraßer, 2015, submitted).

1.5. Radiative forcing and climate impact of contrails

The radiative forcing of a single contrail is calculated as the difference of the net radiation flux (longwave plus shortwave) at the top of the atmosphere of a situation with and without the contrail. This difference depends both on contrail properties and on the the ambient situation, including albedo of the ground, presence of other clouds, sun angle, etc. The radiative forcing as given in IPCC reports is the annual or multiannual average of single-contrail's radiative forcing over the globe. This quantity cannot be measured but is sometimes obtained from measurements of single contrails as a coarse extrapolation (e.g. Voigt et al. 2011). Usually it is the result of global modelling (e.g. Burkhardt and Kärcher 2011), which also allows to study geographic influences, uncertainties originating from model assumptions and inventory differences, as well as visibility thresholds of human eyes and satellite instruments.

1.5.1. Radiative forcing of single contrails

It would be very interesting to compare the radiative forcing of a kerosene contrail with that of a biofuel contrail in the same situation, but such measurements are currently not available. Airborne measurements of contrails from alternative fuels (ACCESS campaigns) so far concentrate on the very young contrails and their microphysical properties. The radiation effect of a single contrail must ideally be determined over a longer time period. Airborne measurements of older contrails or even contrail cirrus are extremely challenging because these old contrails can hardly be distinguished in flight from natural cirrus. It is however possible to track contrail evolution using satellite imaging and to retrieve their radiative properties (see chapters 25 and 26 in Schumann, 2012). Satellite tracking also allows producing a large set of observations such that the sample size gets sufficiently large for a good statistics. More on an experiment strategy to determine radiative effects of single contrails (produced from kerosene vs. alternative fuels) is presented in Section VII. Otherwise we can rely on the results of model simulations of single contrails which also allow studying a large manifold of situations and conditions (chapter 33 in Schumann, 2012).

1.5.2. Global radiative forcing after a hypothetical complete transition to biofuels

There is so far just one global simulation of the radiative forcing and climate impacts from alternative fuels in aviation; it formed part of a doctoral thesis (L. Bock, 2014). The goal of this simulation was rather to explore which climatic benefits are possible at all than to provide a realistic result for realistic scenarios of biofuel introduction into the market (if there are such scenarios at all). Thus, the simulation was based on a purely hypothetical instantaneous transition of (near) present-day air-traffic (based on the AERO2k inventory, Eyers et al., 2004) to alternative fuels. The type of the fuel was not specified; instead it was assumed as a hypothetical effect of the alternative fuel that the initial ice crystal concentration in every contrail was reduced by 80% relative to the corresponding contrail resulting from burning kerosene. This is a very strong reduction which might be unrealistic for certain conditions (c.f. the results of Kärcher and Yu, 2009), but which is justified for the purpose of exploring the space of possibilities.

Compared to the kerosene case, the contrails and contrail cirrus resulting from this hypothetical alternative fuel have larger crystals, less ice mass (25-50%), and lower optical thickness; the contrails get earlier optically thinner than in the kerosene case, leading to strong reductions of the fractional coverage of the visible contrails. Most importantly, the climate effect, that is radiative forcing, is strongly reduced by about 60% (similar reductions occur both in the longwave and the shortwave components).

These results demonstrate in principal a large potential of alternative fuels to reduce the climate impact of contrails, but there remain large uncertainties. It is quite probable that the 60% reduction in radiative forcing will never be achieved in reality. Alternative fuels will gradually be introduced into the market, not instantaneously; the reduction of the initial ice crystal concentration will often be less than the assumed 80% (in particular under cold conditions); ice sublimation in the vortex phase and Ostwald ripening in contrail-cirrus cores lead to loss of small crystals, such that initial differences of crystal concentrations get reduced over time. More realistic estimates of benefits from alternative fuel's effects on contrail properties need scenarios of the penetration into the market and improved representation of such contrails and their variability in climate models. This requires simulations of contrails from alternative fuels with contrail resolving models in order to derive the necessary parameterisations for climate models.

Lisa Bock and Ulrike Burkhardt presented on the mentioned TAC4[11] conference two further simulations with 50 and 90% reduction of initial ice crystal number. The climate benefit of such reductions is given in the following Table 1-1:

Table 1-1: Initial reduction of contrail ice crystal concentration due to an assumed complete transition to biofuels and corresponding reduction of radiative forcing.

Assumed reduction of initially formed ice crystals (%)	Approximate reduction of climate impact (measured as RF) relative to present fleet using kerosene (%)
50	20
80	60
90	70

[11] Transport, Atmosphere and Climate conference 4, Bad Kohlgrub, Germany, 22-25 June 2015

These results show that an expected climate benefit from using alternative fuels depends nonlinearly on the reduction of initial ice crystal formation, with a “slow start”. This suggests that quite substantial ice crystal number reduction is required to produce a significant climate benefit. The results are not yet published.

At the TAC4 conference a new study on contrails from alternative fuels conducted at the MIT has been presented as well (Barrett, Speth, Caiazzo). The study is the PhD thesis of Fabio Caiazzo. It treats contrails over the contiguous USA and finds essentially that a transition from kerosene to alternative fuel has essentially no effect on the resulting radiative forcing, although the impacts on crystal concentration, crystal size, and optical thickness are as expected. Thus, so far the MIT and DLR results seem to be contradictory, but we do not know yet the reason. The MIT study is not yet published, thus a detailed comparison of the two methods and involved assumptions is not yet possible.

Schumann et al. (2013) tested the climate impact of changes to the initial contrail ice number concentration in the other direction — they assumed a doubling, motivated by the results of Stettler et al. (2013 b) on the relation between smoke number and actual soot emissions (see below, section 5.2). A doubling of ice crystal concentration in all contrails worldwide would lead to an increase in global contrail radiative forcing by 64%. This result could thus be taken to extend the entries in Table 1-1 in the opposite direction. It shows the same tendency as the results of Bock and Burkhardt.

1.6. Geographical variances

There are no differences regarding contrail formation from various fuels that are enhanced or diminished depending on geographic location.

However, individual contrails are most warming (have the highest individual radiative forcing) when they are formed over warm and bright surfaces, like a sand desert. It may be possible that use of biofuels primarily in such regions has a larger beneficial effect than in regions where cold and dark surface predominates, e.g. over high latitude open sea water surfaces. Nothing is known so far on such geographical variances of the climate benefit of a transition to biofuels. Simulations that would show such effects do not yet exist.

2. Pareto assessment, most likely causes, variability

The term Pareto assessment is understood here as an enumeration of the different parameters that influence contrail formation (i.e. thermodynamic, soot and volatile particles), ranked by the magnitude of their contribution to contrail formation, as agreed with the Commission.

2.1. Parameters that affect contrail formation

Contrail formation is governed by thermodynamics and dynamics exclusively, which is expressible as the Schmidt-Appleman criterion (Schmidt 1941, Appleman 1953); this criterion follows from fundamental physical conservation laws of energy and momentum; a detailed derivation is given in Schumann (1996). The Schmidt-Appleman criterion states that contrail formation occurs whenever the relative humidity in the expanding plume (which thereby is mixed with cold ambient air) transiently reaches and exceeds water saturation (i.e. relative humidity, RH≥100%). Water saturation is given when the water vapour pressure equals the saturation vapour pressure which in turn depends on temperature. Thus the Schmidt-Appleman criterion is best viewed using a diagram showing temperature and water vapour pressure in the expanding plume, see Figure 2-1.

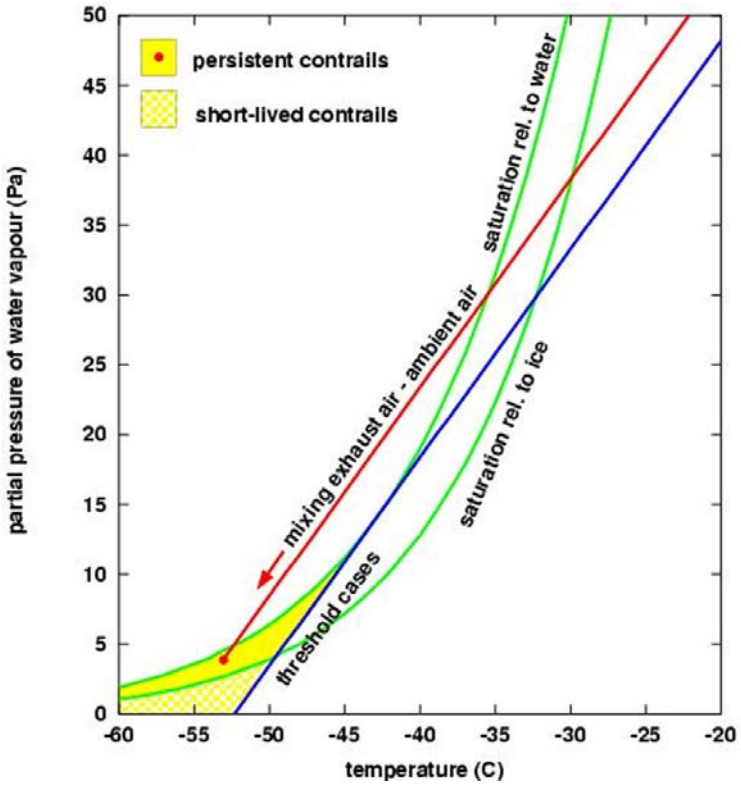


Figure 2-1: Schmidt-Appleman diagram showing partial pressure of water vapour versus temperature in an expanding exhaust plume (red or blue) together with curves showing saturation vapour pressures with respect to liquid super-cooled water and ice, respectively (green curves). The blue line marks threshold cases for contrail formation, that is, cases where water saturation is just achieved during expansion. Contrails can only be formed if the ambient air is represented by a point in the area left of the blue line in the area marked yellow. The red dot is an example of such a point, and the red line thus represents a case where contrail is indeed formed. Climate affecting are only contrails above the ice saturation curve, where contrails would be persistent. The red point represents such a case.

As the figure shows, for a given ambient situation (temperature and vapour pressure), the probability of contrail formation increases with the steepness of the mixing line, G:=de/dT (where e is partial pressure of water vapour and T is temperature). According to Schmidt-Appleman theory, G (Pa/K) is given by the following equation:

$$G = \frac{c_p p}{\varepsilon} \frac{EI_{H2O}}{(1-\eta) LHV}$$

In this equation, c_p=1005 J/K is the specific heat at constant pressure of air, p is air pressure at the flight level, ε=0.622 is the ratio of the molar masses of water and air. η depends on engine and combustion; it is the overall propulsion efficiency. EI_{H2O} and LHV are fuel characteristics and thus the only parameters that can be affected by a transition from kerosene to alternative fuels; they are the emission index of water vapour (kg water vapour emitted per kg fuel burnt) and the lower heating value of the fuel (MJ per kg of fuel).

The temperature, T_{max}, at which the (blue) mixing line in the Schmidt-Appleman diagram is tangent to the water saturation curve, is the highest temperature where a contrail can be formed. One effect of higher H/C in alternative fuels is a slight increase of T_{max}, since H/C implies higher EI_{H2O}/LHV and thus higher G (a steeper mixing line). This is detailed in Section 3.2.

Another effect of a higher T_{max} is that cases that are threshold cases when kerosene is used are no longer threshold cases when alternative fuel with higher G is used. At the threshold the number of ice crystals forming from soot particles increases sharply with distance to the threshold (measured either by the difference of the ambient temperature to the corresponding temperature on the threshold mixing line at the same vapour pressure or by the maximum water supersaturation, i.e. the ratio between the vapour pressure at T_{max} and the water saturation pressure at T_{max}; see Kärcher et al. 2015, e.g. their table 2). In such cases it is indeed possible that a contrail formed from alternative fuel burning has actually higher ice crystal concentration than a contrail formed from burning kerosene. It is unknown how important such cases are since a statistics of how frequently contrails are formed just at the threshold (relative to a few degrees below the threshold) does not exist. Such a statistic would be worth to be set up.

2.2. Parameters that affect contrail properties

The most important parameters that affect contrail properties are ambient meteorological conditions, in particular temperature, relative humidity (supersaturation), and wind shear (the variation of wind speed and direction with altitude across the contrail's depth). Contrails' individual climate impact furthermore depends on ambient cloudiness, surface albedo, and position of the sun (in particular night or day). These external conditions are so influential that individual contrails can induce cooling and warming of the atmosphere at very high rates, say from –50 W/m² to +50 W/m². These values are about thousand times higher than the global average radiative forcing of contrails and contrail cirrus (which is of the order, say, 50 mW/m²). This enormous range of individual forcing and the overwhelming influence of the current ambient situation on it mean that two kerosene contrails formed by the same engines under different conditions (e.g. night vs. day, or cloudy vs. clear) can differ much more than a kerosene contrail from a contrail formed by alternative fuel when they are located in the same environment.

The impact of the fuel type on contrail properties is caused by the differences in emissions of particles (soot and volatiles, but mainly soot) and water vapour. Although the ~10% higher water vapour emission of alternative fuels has an effect on contrail formation close to the Schmidt-Appleman threshold (see section 2.1), its influence on contrail properties under off-threshold conditions is negligible because eventually most (that is almost 100%) ice a contrail cirrus is composed of is taken from ambient water vapour in excess of ice-saturation. The emitted water only contributes a very minor fraction to the ice mass in contrail cirrus.

The number of soot particles emitted is most important for contrail properties since, at current emission levels, it determines the number of ice crystals formed, which in turn affects contrail optical thickness and microphysical development. In the same ambient situation a contrail consisting of less ice crystals will have larger ice crystals that earlier commence to fall into lower altitudes (and vice versa). As sedimentation is one of the processes that terminates the lifetime of contrails, contrails consisting of less crystals will last shorter than contrails consisting of more crystals. However, there are synoptic situations where this difference doesn't matter, namely when the ambient atmospheric dynamics forces the airmass containing the contrail to move downwards. In such cases contrails are terminated by adiabatic heating caused by that dynamic forcing. Which termination process is actually dominant in the atmosphere, is not yet known and should be investigated.

2.3. Uncertain aspects that justify further research

a) Lower soot emissions, both by mass and by number leads to contrails with less ice crystals relative to kerosene. This can have strong benefit for climate if the soot reduction by number is strong (>50%). If soot is reduced by factors of 100 or even 1000, for instance when alternative fuels are used in combination with lean combustion, then volatile particles and particles entrained from the ambient atmosphere into the expanding plume take over ice formation. At conditions close to the formation threshold (i.e. close to the blue line in Figure 2-1) the resulting ice crystal number will obtain a minimum that cannot be further reduced by further reductions of soot emissions (see Figure 1-3, top and middle panel). However, under conditions sufficiently below the formation threshold, further reduction of soot leads to increasing ice number concentrations. As stated before, a study should be undertaken to determine the relative frequencies of threshold, near-threshold and far-below-threshold conditions in order to gain a feeling of how important these different scenarios are.

Such a study would be informative as well for the questions of how important threshold effects are, like sulphur coating of soot particles, potentially different soot surface properties resulting from kerosene vs. alternative fuel burning, higher H/C.

b) The impact on climate might be a significant benefit (regarding contrail RF), but large reduction factors of ice crystal number concentrations are needed for a significant gain. However, as mentioned, simulation results from the MIT group contradict those of the DLR group in that essentially no benefit in terms of reduced RF is calculated for a transition to alternative fuels. The reason for this discrepancy is so far unknown as the American study is not yet published. One point to observe is that general conclusions need a sufficient statistical basis because of the tremendous natural variability. In Lisa Bock's thesis the transition to alternative fuels with an assumed 80% reduction of initial ice crystal number concentration in contrails led, as expected, to a strong reduction of the average contrail optical thickness (-35% for young contrails and -26% for contrail cirrus). Although these reductions are quite substantial (and contribute eventually to the strong and statistically significant -60% reduction of radiative forcing) they are not statistically significant at a 5% level, in spite of ten years of simulation. This means that there is a huge year-to-year variation of optical thickness reductions; the average of ten years is still not robust (although its sign is), and if such a study would be done for a single year only, the result must be more or less random, that is, it is not representative at all for the climate impact. Thus it is necessary to conduct simulations of many years in order to achieve robust results.

c) A further open question is why the climate benefit resulting from a transition to alternative fuels seems to depend non-linearly (i.e. non-proportionally) on the reduction factor of soot emissions, that is "why is a substantial soot reduction

necessary for a substantial climate benefit and why is a minor or moderate soot reduction insufficient?"

d) It is so far also unknown whether climate benefits from a transition to biofuels are different in the mid-latitudes and the tropics. Such dependence is well conceivable as the natural conditions that affect individual contrails and that lead to the huge variation of their individual radiative forcing differ in different climate zones. Knowledge of such effects could result in recommendations to use biofuels primarily in certain climate zones (for instance, if a sufficient amount of biofuels to feed the whole world fleet cannot be produced). This is a question that could be studied best with a small-scale model capable to simulate single contrails in various backgrounds.

3. Identification of fuel and combustion system related parameters

In previous sections, the relationship between aero-engine's emissions in high altitude, contrail formation, and climate has been described and analysed. The objective in the following section is to describe what is happening upstream the engine plume, from the kerosene liquid fuel delivered at the airport to the hot gases leaving the engine combustion chamber.

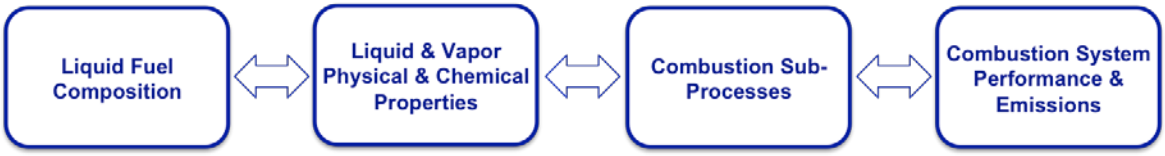


Figure 3-1: Flow chart from kerosene to engine performance and emissions.

Figure 3-1 above shows that the hydrocarbon families composing the kerosene as well as the number, the nature, and the volume fraction of pure components in each family affect the specific fuel physical and chemical properties. These properties are in turn directly controlling the onset and the magnitude of key combustion sub-processes, which are relevant to combustion system performance, emissions and, atmospheric impact.

3.1. Interaction between composition and performance of jet fuels, biofuels and kerosene/biofuel blends – physical and chemical properties

3.1.1. Fuel composition – Fuel properties

The chemical composition (also denoted as formulation) of any fuel (conventional kerosene as well as biofuel blends) determines its physical and chemical properties. In an ideal case, these properties are known for each pure species composing the final jet fuel mixture and the mixing rules are also known. Note that depending on the property under consideration, a simple arithmetic average is not always the most accurate mixing rule. For example, while under normal conditions, the final density of a fuel blend is linearly dependent (i.e. arithmetic mixing rule) upon the density of each blend stock and upon the blending ratios; this is not true (i.e. non-linear behaviour) for other properties such as the viscosity or the freezing point. This was also noted in the EU-ENER HBBA 2012 study.

Physical Fuel Properties – Combustion System Sub-Process Quality

First, it has to be underlined that all the sub-processes listed below are highly dependent upon the local temperature, pressure and often flow dynamics properties.

The overall performance of a combustion system, including volatile and particulate emissions depends upon many sub-processes. While some of these sub-processes are mostly related to engine geometry/hardware or gas turbine aerodynamics, several are actually dependent upon the liquid fuel properties. These liquid-fuel dependent sub-processes are here of interest, as we are aiming at deriving the fuel and combustion system related parameters. The fuel placement in the primary zone of the combustion chamber is one of those sub-processes. Actually, it can be separated into two sub-processes: atomization (primary and secondary) and evaporation.

Atomization depends on the following physical properties: liquid viscosity, surface tension, and liquid density.

Evaporation depends on the following physical properties: liquid density, vapour pressure, latent heat of vaporization, liquid and vapour heat capacities, vapour thermal conductivity, vapour viscosity, vapour mass diffusion coefficient.

In a combustion system, the ignition, flame stabilization as well as flame blow-off also depend upon fuel placement plus specific chemical properties such as the ignition delay time or the laminar flame speed, which are both strong functions of the combustion kinetics. Moreover, the lower heating value of the fuel and the H/C ratio (both are correlated) have a direct effect on the local heat release during the fuel vapour oxidation. This in turn also affects the above mentioned sub-processes.

The emissions also depend strongly on fuel placement, i.e. on specific species concentrations, temperature, pressure, and fuel-air ratio.

Chemical Fuel Properties – Combustion System Sub-Process Quality

Amongst the chemical properties, the effects of real fuel composition on the gas-phase-relevant kinetics, which also controls combustion performance and most importantly emissions, cannot be fully addressed in the similar manner as the physical properties. Actually, the compositional complexity of conventional or alternative fuels creates a true challenge in terms of combustion kinetics. The main difficulty is in how to reduce the description of any complex fuel-mixture combustion kinetics, which involves hundreds of relevant intermediate species and products and thousands of elementary reactions, while continuing to capture all the important fuel-specific features and differentiate between two similar but complex jet fuel mixtures. Of course, first a detailed reaction mechanism must be elaborated in a smart way, thus that a reduction of the huge scheme is feasible without losing needed accuracy in the description of the fuel's combustion.

For the purpose of modelling and computing combustion system sub-processes, there are certain reduction strategies available for those reaction mechanisms. For the purpose of interpreting the impact of the kinetics of thousands of elementary reactions on the overall emissions a more pragmatic way is needed. Concerning emissions, the present practical way consists in looking at the impact of certain hydrocarbon families composing a jet fuel on specific pollutant or particulate emissions. The typical jet fuel (from crude oil) is primarily composed of alkanes (e.g. paraffins: normal, iso, and cyclo), aromatic compounds (alkyl benzenes, indanes, tetralins, naphthalenes and indenes) and hetero-molecules (non-hydrocarbons in very small quantities) amongst which some contain sulphur atoms. Many Alternative Fuels do not contain aromatic compounds; in addition, sulphur atoms are not included in Alternative Fuels due to the production process.

3.1.2. Combustion system sub-processes – Emissions

The sulphur content of a jet fuel has a direct impact on SO_2 and SO_x emissions (pollutants, e.g. acid rains). More generally, even in very small quantities (sulphur content is typically measured in ppmm, with a present average value in Western countries between 600 – 1000 ppmm) the sulphur content affects the emission index (EI, number and mass based) of aerosols. Reducing the fuel sulphur content to near zero results in a 10- to 100-fold reduction in aerosol number EI with the greatest reduction observed at intermediate to high engine powers (Moore et al., 2015).

The aromatics content of a jet fuel has a direct impact on soot emissions (also called black carbon or particulate matter PM or, non-volatiles, see Petzold et al 2013 for terminology). This has been demonstrated during the APEX, AAFEX and ACCESS measurement campaigns.

Up to now, rig tests have not shown a direct link between the fuel composition and NOx (nitrogen oxides) or UHD (unburned hydrocarbons) emissions. The EU FP5 ALFA-

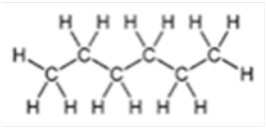
BIRD Project as well as the SWAFEA study both have actually shown that this is more dependent upon the combustion system architecture and engine settings.

3.1.3. Fuel energy content – Aircraft performance

While we have seen a direct and traceable link between some chemical families composing the liquid kerosene and specific emissions, there is also an indirect link that should be accounted for. The overall energy content of the fuel will affect the aircraft fuel consumption thus it will affect the total quantity of pollutants left in the atmosphere and to a lesser extent in the airport vicinity. In other words, the less fuel it takes to carry a certain number of passengers or freight, the less pollutants, at least with respect to CO_2, are in the atmosphere.

The metrics, which is relevant in that respect, is the energy content of the fuel (Hileman *et al*, 2010). More specifically, the energy per unit volume: energy density (MJ/L), on one side and the energy per unit mass: specific energy (MJ/kg), on the other side. The ASTM D1655 Specifications for aviation turbine fuels sets a requirement in terms of a minimum specific energy (or net heat of combustion), which is 42.8 MJ/kg. From an airline standpoint, the two main aircraft parameters, which depend on the energy content, are the range and the maximum takeoff weight (MTOW) as they translate into economic factors. The higher the range the further an intercontinental flight can go and the higher the MTOW the higher the payload (passenger, freight) the aircraft can carry. All else being equal, the relationship between energy content and aircraft parameters is the following. For a route, which is range-limited, the airlines would want to put as much energy as possible in the limited volume the aircraft tanks offer. In such a case, fuels with a high amount of energy per unit volume, i.e. high energy density is ideal. For a short- or medium-haul flight the limitation comes from the MTOW and airlines would want to carry as many passengers (or freight) as possible. In such a case, fuels with high energy per unit mass (specific energy) are ideal.

By definition, SPK synthetic fuels (e.g. FT-SPK or HEFA) are composed solely of n-alkanes, iso-alkanes, and cyclo-alkanes. Another nomenclature to group these families is paraffinic compounds. From a molecular structure analysis, one only needs to know that alkanes are linear molecules (see Figure 3-2 left) whereas aromatics are ring molecules with delocalized ∏-electrons (Debye-Hückel) (see Figure 3-2 right). Consequently, for a given number of carbon atoms (for example 6 carbons in both molecules schematically represented in Figure 3-2), paraffins pack more carbon-hydrogen bonds (this is where the chemical energy is stored, with triple bonds stronger than double and simple carbon hydrogen bonds) with respect to aromatics. In the example displayed in Figure 3-2, there are 14 C-H bonds in the n-hexane molecule and only 6 C-H bonds in the benzene molecules, with 3 C-H and 3 C=H bonds, respectively. Moreover, since the carbon atoms have a molar mass 12 times higher than the hydrogen atoms (12 g/mol and 1 g/mol respectively), for a given number of carbon atoms both molecules have similar weights yet the linear molecule packs more energy. Although this is obviously a simplistic view, it explains why paraffins have higher specific energy with respect to aromatic molecules. On the other hand, linear molecules are stretched much more than ring molecules so that they have a lower energy density (less energy per unit volume).



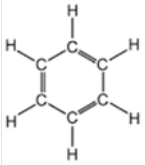


Figure 3-2: Molecular structure. Left: normal paraffins, here n-hexane C_6H_{14}. Right: aromatic compounds, here benzene C_6H_6.

In summary, for a given number of carbon atoms, paraffinic compounds have a higher specific energy (MJ/kg) than aromatic compounds and aromatic compounds have a higher energy density (MJ/L) than paraffinic compounds. Actually, this simplistic analysis applies also to average values of the jet fuel energy content. SPK fuels (no aromatics) have higher specific energy and lower energy density relative to conventional jet fuel, which has a content of aromatic compounds comprised between 8 vol% and 25 vol% according to the specifications.

The abovementioned concepts define an important relationship between fuel properties, aircraft performance and overall emissions, and economics. In reality, the payload-range relationship is governed by a more complex and non-linear equation. Aircraft manufacturers and airlines use the Breguet range equation to define the operability of the aircraft during cruise.

$$R = -\frac{VL/D}{g \cdot SFC} \ln\left(\frac{W_1}{W_2}\right)$$

The Breguet range equation defines how far (R: range) an aircraft can fly given a certain set of parameters: VL/D the flight speed V times the lift-to-drag ratio L/D, W_1 and W_2 are the initial and final weights during cruise and, SFC is the specific fuel consumption define as the fuel mass flow rate (in kg/s) divided by the thrust (in Newton). For a first order analysis one can see that the range depends on a structural parameter (e.g. empty weight), an aerodynamics parameter (lift-to-drag ratio), an engine performance parameters (SFC), which is indirectly related to the fuel through its energy content and also more directly on the fuel density in W1, as the difference between W_1 and W_2 (during cruise) is mostly the fuel consumed. How does it translate in practice? Actually, one of the major findings after 1187 scheduled revenue flights from the German airline Lufthansa between Frankfurt and Hamburg (burn-FAIR) is that the fuel flow rate of the engine powered by the 50% HEFA-blend was about 1% less than that of the engine powered by conventional jet fuel. Less fuel was consumed because pilots follow the procedure and order the fuel in mass. For the typical fuel tonnage needed to cover that distance, which was calculated according to the daily payload having more energy per ton of fuel translates into setting a lower fuel mass flow rate to reach the same thrust. From an economics perspective this is already of great benefit.

A different benefit could be to actually increase the payload knowing that the fuel on board has a higher specific energy. For safety reasons, in practice only the minimum values given by the requirements stated in the jet fuel specifications are used. If tomorrow all aircraft would fly on a 50% blend of approved SPK (FT-SPK or HEFA-SPK), and although more than 50% of these flights are MTOW-limited, since there is no on-line measurement of density and energy content, operations would still be defined by the minimum requirements thus not enabling airlines to take advantage of the extra payload they could carry on the same route by using fuels with higher specific energy.

3.2. Impact of fuel and combustion system related parameters on contrail formation and contrail properties

Aircraft engine emissions have an impact on contrail formation and contrail properties. Contrail formation can be described by the so-called Schmidt-Appleman criterion, whereas contrail characteristics in terms of optical depth and cover depend on particle properties and ice water content (Schumann, 2005). Within the plume of an aircraft, hot and moist exhaust gases from the engine are mixed with cool ambient air. Whereas the temperature and speed profiles of the core and the bypass stream are different at the engine exit plane, the so-called jet becomes a uniform turbulent flow a few engine diameters behind the engine exhaust. As a result, the relative humidity (RH) is increased and visible line clouds may occur, due to the formation of liquid droplets, when liquid saturation is reached. According to the Schmidt-Appleman criterion the ambient threshold temperature below which contrails form depends on ambient RH and the parameter G

$$G = \frac{EIH_2O \cdot p \cdot c_p}{\varepsilon \cdot LHV \cdot (1-\eta)}$$

where p is the ambient pressure, c_p the isobaric heat capacity of air and ε the ratio of molecular weight of water and air. Alternative drop-in fuels have a direct impact on water vapour emission index EI_{H2O} and lower fuel heating value LHV due to changes in jet fuel chemical composition. The overall efficiency of the propulsion system η is mainly dependent on engine design, but may also be influenced by biofuel combustion. The threshold temperature for 100% relative humidity (saturation with respect to liquid water) can be calculated from

$$T_m = -46.46 + 9.43 \cdot \ln(G - 0.053) + 0.720 \cdot [\ln(G - 0.053)]^2$$

A sensitivity study has been conducted to identify the dependencies of these parameters on the threshold temperature, for various ambient relative humidities, exemplary at altitude of 10000 m.

Aircraft engine emissions of water vapour (H_2O) and carbon dioxide (CO_2) are the main combustion products of burning hydrocarbon fuels with air. Water vapour emissions correlate with the amount of hydrogen within the fuel and hence are coupled to fuel consumption. An emission index (EI) specifies the amount of emissions per kg of fuel. Assuming a pure hydrocarbon fuel (e.g. neglecting sulphur content) and complete combustion the emission index of H_2O can be derived from the following equation:

$$C_mH_n + \left(m + \frac{n}{4}\right)O_2 \rightarrow mCO_2 + \frac{n}{2}H_2O$$

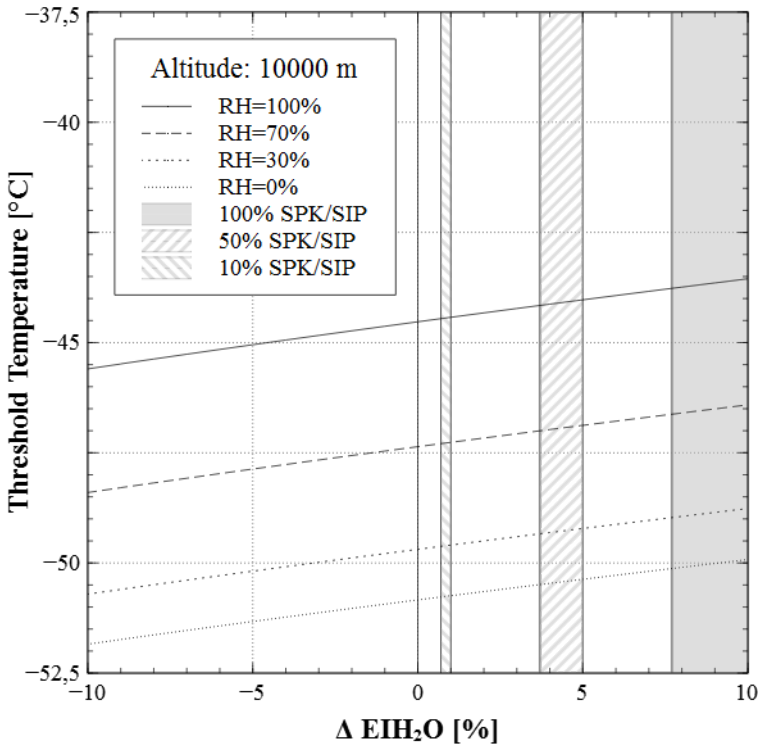


Figure 3-3: Sensitivity of threshold temperature of contrail formation for aircraft engine water vapour emission index ranging from 1.1133 to 1.3607 at altitude 10000 m and relative ambient humidity of 0%, 30%, 70% and 100%.

The hydrogen content of conventional Jet A-1 fuel is not defined within the fuel specification. However, Rachner proposed a typical average hydrogen mass content for Jet A-1 of about 13.9% (Rachner, 1998). The emission index of water vapour EI_{H2O} for conventional jet fuel is about 1.237 kg/kg (Sutkus et al., 2003). Alternative SPK or HEFA jet fuels have a slightly different chemical composition. Neat SPK or HEFA fuels are virtually free of any aromatic compound and therefore reveal a higher hydrogen mass content of about 15% to 15.5% (Kinder et al., 2009; Hileman et al., 2010) and hence, the EI_{H2O} is increased to about 1.36 kg/kg. The impact of the water vapour emission index EI_{H2O} on the threshold temperature for contrail formation is shown in Figure 3-3.

The deviating chemical composition of alternative fuels results in a different thermodynamic behaviour in terms of burned gas properties and energy content. The jet fuel specification defines a minimum value for the energy content of the fuel of 42.8 MJ/kg. Fuel sample analyses show typical average heating values for conventional Jet A-1 of about 43.3 MJ/kg (Rachner, 1998; Hileman, 2010; PQIS, 2009). Alternative SPK or HEFA jet fuels have higher energy content in the range of 44-44.3 MJ/kg (Kinder et al., 2009; Hileman et al., 2010). Figure 3-4 depicts the threshold temperature as a function of fuel heating value.

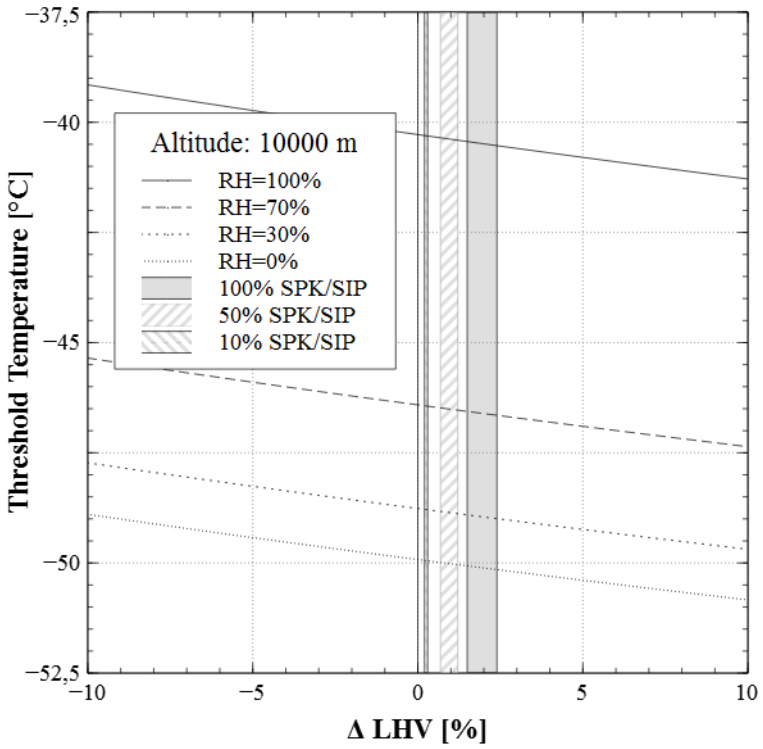


Figure 3-4: Sensitivity of threshold temperature of contrail formation for fuel lower heating value ranging from 38.9 MJ/kg to 47.6 MJ/kg at altitude 10000 m and relative ambient humidity of 0%, 30%, 70% and 100%.

The chemical composition of the fuel and hence the properties of the burnt gases, respectively, may have an impact on the efficiency of the engine. Higher water vapour emissions increase the isobaric specific heat capacity of the gas, which is expanded through the turbines of the engine. The power output W of the turbines is proportional to the isobaric heat capacity:

$$W = c_P \cdot (T_2 - T_1)$$

Consequently a higher isobaric specific heat capacity raises the power output of the turbines and thus improves the overall jet engine cycle.

However, in terms of drop-in alternative fuels, these changes can be neglected (Wolters et al., 2012) and the overall engine efficiency is affected by engine design. The corresponding impact on the threshold temperature can be seen in Figure 3-5.

Since the impact of fuel heating value and emission index of water vapour is in the opposite direction, the resulting effect on threshold temperature is shown exemplary for a typical Jet A-1 and neat SPK fuel in Figure 3-6. The relevant parameters are listed in Table 3-1.

Table 3-1: Typical values of conventional Jet A-1 and neat SPK fuel relevant for contrail formation.

	Jet A-1	**SPK**
LHV [MJ/kg]	43.3	44.2
EIH_2O [kg/kg]	1.237	1.36

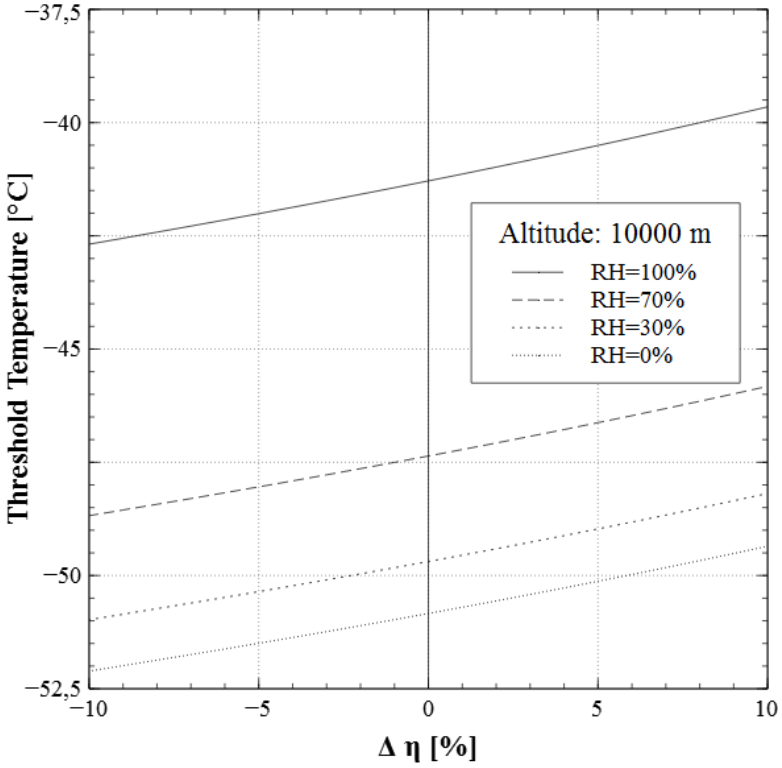


Figure 3-5: Sensitivity of threshold temperature of contrail formation for engine overall efficiency ranging from 0.2 to 0.4 at altitude 10000 m and relative ambient humidity of 0%, 30%, 70% and 100%.

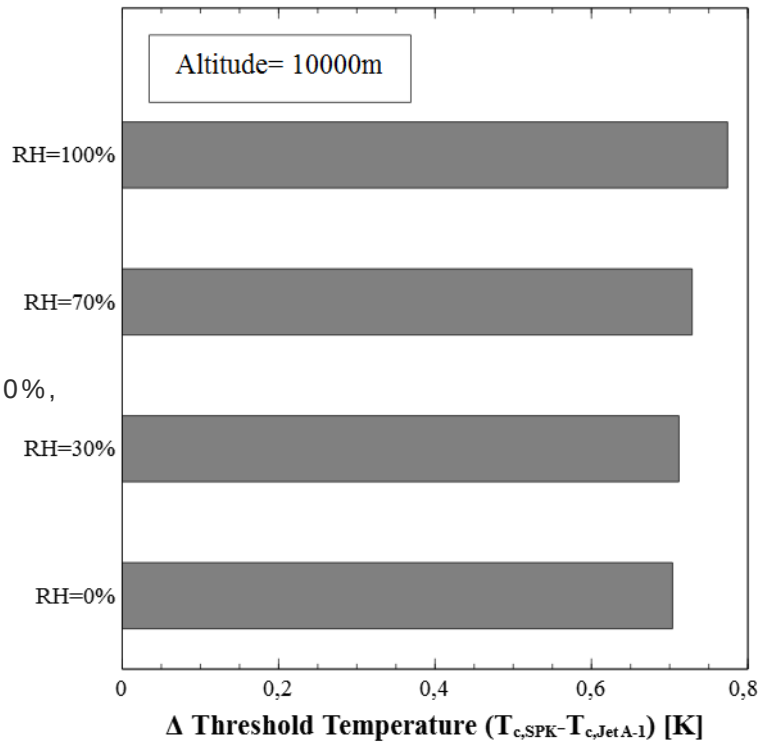


Figure 3-6: Threshold temperature changes for using neat SPK fuels compared to conventional Jet A-1 at altitude 10000 m and relative ambient humidity of 30%, 70% and 100%.

According to Kärcher and Yu (2009) contrail optical depth could potentially be reduced by reducing the number of available ice condensation nuclei in a contrail. Condensation nuclei within aircraft engine plumes may be affected by the emissions of particles (Particulate Matter), which mainly consists of soot (or black carbon). However, sulphur oxides emissions may also act as ice crystal nuclei. Due to the fact that alternative fuels are virtually free of any contaminant (e.g. sulphur), sulphur oxides emissions are expected to be reduced significantly.

The complex process of soot formation depends on fuel parameters, e.g. content of aromatic hydrocarbons, but also on combustion system design and the operating condition of the engine. The soot concentration at engine exit plane is the difference between two large numbers: Soot formation in fuel-rich zones close to the fuel spray and soot consumption. Consequently the resulting soot concentration and particle size distribution cannot be easily related to specific parameters. However, the rate of soot formation may depend on fuel atomization and fuel-air mixing [Levebvre and Ballal 2010]. According to Döpelheuer (2002), combustor inlet temperature and pressure, as well as the equivalence ratio and flame temperature are characteristic parameters to describe soot concentrations. The method is based on sea level static reference data and therefore takes the specific combustor design into account.

3.3. Conclusion and Summary

Contrail formation and properties are affected by aircraft engine emissions. Whereas the threshold temperature for contrail formation can be described by the so-called Schmidt-Appleman criterion, contrail characteristics in terms of optical depth and cover depend on particle properties and ice water content.

Alternative jet fuels, yet certified for use in aviation, have a slightly different chemical composition and are virtually free of any aromatic compound. Therefore these fuels reveal a higher hydrogen content and higher energy content (in terms of specific energy, MJ/kg). To quantify the effect on contrail formation a sensitivity study has been conducted. Due to the opposing effect of water vapour emission index and fuel heating value the resulting change of threshold temperature is below 1 K and therefore not significant. For comparison, the International Standard Atmosphere gives a temperature lapse rate of –6.5 K per km.

4. Comparison of physico-chemical properties of fossil fuel based fuels and biomass based fuels

For the past fifty years, the commercial jet engine fuel (Jet A-1 in Europe, Jet A in the US) has been developed as a whole, focusing on safety and performance within the entire flight envelope. In other words, the kerosene cut from oil refineries was optimized to meet turbine fuel specifications, which were also developed in parallel. With the exception of very few approved additives, it was never a species-by-species development but rather a cut in the bulk. Therefore, comprehensive knowledge has not been reached when it comes to how certain families of compounds or single species within conventional jet fuel affect specific properties (chemical and physical) and consequently how they impact the engine performance and emissions, the aircraft systems and/or the ground handling and safety. Moreover, certain families of compounds (e.g. sulphur containing molecules) naturally occurring in refinery products and often detrimental in terms of emissions are not needed to fulfil safety requirements or the amount of some other molecules (e.g. aromatics) can be reduced to a minimum (even none) which is not attainable in crude-oil refined jet fuel. Synthetic fuels on the other hand offer the possibility to derive an alternative fuel species-by-species, which could rid kerosene fuel from detrimental compounds, provided the final blend complies with fuel specifications.

As Jet A-1, alternative aviation fuels are also composed of hydrocarbons; however, amount and type of hydrocarbons (chemical family) differ considerably, see e.g. Figure 4-1 (Edwards et al., 2010). It is an open question how the properties of a fuel, i.e. its chemical nature, affects its suitability and performance.

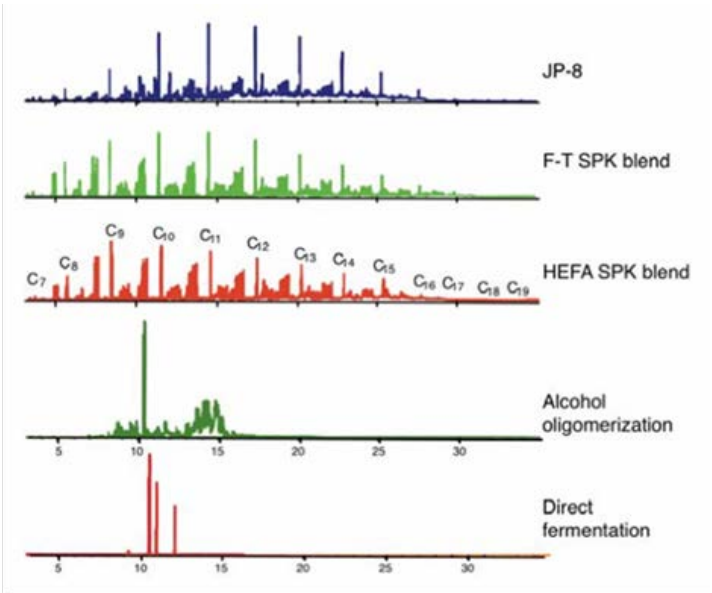


Figure 4-1: Gas chromatograms of approved jet fuels and near future candidates, Edwards et al., 2010.

The properties and involved sub-processes identified are discussed. Fuel placement and fuel's combustion play a pivotal role to ensure the fuel's suitability and applicability. Selected properties of the components a jet fuel might be comprised of are given exemplarily.

Thermo-physical properties are discussed, with the focus to exclude any failures with respect to performance and safety issues. Concerning thermo-chemical properties, the focus is on the fuel's combustion characteristics, with auto ignition, flame speed, and emission pattern (pollutants), in particular, to guarantee a less harmful impact on the environment.

Challenges are considered to exist resulting from the complexity of a fuel. This suggests the deployment of numerical tools that must enable to describe the thermo-physical and thermo-chemical properties of a fuel as well as the detailed processes occurring during the fuel's placement (thermo-physical properties) and the fuel's combustion (chemical properties). The prerequisites needed are addressed.

4.1. Fuel-dependent physical sub-processes for biofuel and kerosene / biofuel blends

Two levels should be considered in this chapter. First level concerns the jet engine as a whole and how the fuel type can affect the thermodynamic efficiency of a gas turbine. The second level is more concerned with the details and how the fuel composition affects individual physical sub-processes occurring in the combustion chamber of a gas turbine.

The fuel composition affects the thermodynamic parameters and running conditions characterizing a gas turbine. In particular, the amount of chemical energy stored in the fuel (quantifiable by the lower heating value) and the temperature reached when releasing that energy (quantifiable for example with the adiabatic flame temperature, which is an idealization of the temperature that the products of the combustion reaction would attain if no heat was lost, also indirectly given by the H/C ratio) are modified when adding new molecules (for instance farnesane) and/or when changing the relative concentration of the different hydrocarbon molecules . These in turn affect the overall thermodynamic efficiency, the liner thermal loading or, the turbine inlet temperature. Bester and Yates (2009) conducted experiments on a RR-Allison T63-A-700 turboshaft gas turbine burning 100% SPK fuel and concluded that the lack of aromatic compounds and increased hydrogen-to-carbon (H/C) ratio of SPK fuel led to a 1.2% increase in engine efficiency.

As mentioned in Chapter 3, the fuel placement, which consists in atomization, droplet transport and turbulent dispersion and, evaporation, as well as specific combustor-related sub-processes such as ignition, lean blowout, stability and emissions are dependent upon fuel physical and chemical intrinsic properties. The specific fuel properties, which are known to have a direct effect on these sub-processes, are listed in the Table 4-1 below.

As illustrated in chapter 3.1.3 with the detailed example concerning the fuel specific energy, each fuel property listed in this Table is modified through a change in the fuel composition. Actually, with this table the complexity in the interdependency between composition, fuel property and combustor performance issue becomes very clear. As for the already approved alternative aviation fuels, one should expect that with the development of new pathways and the introduction of new bio-derived molecules, these properties will be modified and an effect on the jet engine performance and emissions will be measurable. This is the main reason why a long and costly approval process (ASTM D4054) was introduced in the first place. The issue of emissions and contrails goes beyond the approval process. It is important to underline here the difference between on the one hand safety and airworthiness, which are assessed through the approval process and on the other hand indirect and long term effect such as a reduction in emissions or in operating costs through the use of premium alternative fuels.

Table 4-1: Main fuel properties relevant for combustor performance issues.

Selected Combustor Performance Issue	Fundamental Processes	Fuel Property
Ignition & high altitude relight	atomization	viscosity liquid density surface tension
	evaporation	liquid density vapour pressure latent heat of vaporization distillation curve liquid and vapour heat capacities vapour thermal conductivity vapour viscosity vapour mass diffusion coefficient
	reaction kinetics	ignition delay time laminar flame speed
Lean blowout	atomization	same as above
	evaporation	same as above
	reaction kinetics	flame temperature extinction strain rate laminar flame speed
Exhaust emissions/combustor efficiency	UHC & CO	All the above properties + H/C ratio
	NO_x	
	Soot	

4.2. Combustion properties – ignition, flame propagation, emission - for biofuel and kerosene / biofuel blends

Aviation jet fuels are composed of numerous hydrocarbons of different chemical groups [Steil et al. 2008, Braun-Unkhoff et al., 2015a, b, Dagaut and Cathonnet, 2006], (Figure 4-2). Synthetic jet fuels can be made from various non-petroleum feedstocks, such as coal, gas, biomass including waste, or industrial by-products. To date, four different kinds of alternative jet fuels are certified. They can only be used in blends, up to 50% depending on the kind of synthesized fuel, with Jet A-1, besides the FSJF produced from Sasol.

Advanced biofuels are the only low-carbon option (reducing CO_2) for substituting kerosene. Synthetic jet fuels that are certified to date contain no fuel-bound nitrogen and almost no sulphur or aromatics, in contrast to crude-oil kerosene. In addition, their H/C ratio might differ considerably. Hence, their emission characteristics are differing when burning these fuels in a jet turbine. Even more, synthetic fuels might offer an emission pattern with a reduced detrimental factor on the environment. However, future jet fuel candidates, including renewables, might contain aromatics in a considerable amount.

The combustion properties are predominantly determined by the fuel's composition and, to some degree, by the fuel placement (governed by physical properties). As part of the fuel's performance, knowledge of major combustion properties such as ignition delay time (safety), laminar flame speed (stability), and emission pattern (pollutants) is required, as a function of fuel components, temperature, pressure, and fuel-air ratio; see [Kick et al. 2011, Kick et al. 2012, Mzé Ahmed et al. 2013, Dagaut et al. 2014].

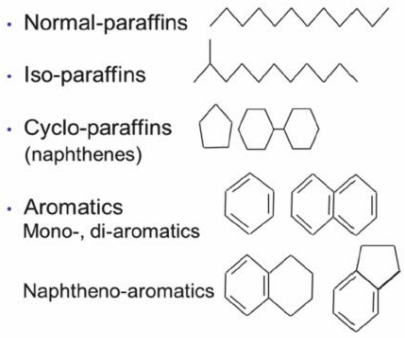


Figure 4-2: Chemical families that may be present in current aviation jet fuels.

Major combustion properties - Aircraft Emissions

Oxidizing a fuel results in the release of energy and emitted products. Kind and amount of emitted products is depending on the fuel/air ratio and thus, on the temperature as well as on the power setting, besides the specific jet fuel's composition. The in-flight emissions (air borne) may affect the climate besides local air quality when released at ground (airport). In particular, they may alter the concentration of atmospheric greenhouse gases and the earth's radiative forcing (RF).

Climate impacts due to emissions of NO_x, H_2O, sulphur, aromatics, and particulate matter (PM), the latter through cloud nucleation, are expressed in terms of global average radiative forcing (RF, units W m^{-2}), see [Lee et al., 2009]. The RF components associated with aviation are given showing the best estimate available and including an estimate as to the confidence level in the data and the current level of scientific understanding [Blakey et al., 2011; Lee et al. 2009].

Thus, valuable information can be gathered when evaluating the contributions of aircraft emissions to the predicted rise in globally averaged temperature or sea level due to global warming.

According to the RF values, (aircraft) emissions mostly show warming effects, with a more pronounced effect when including formation of contrails and of cirrus, as well. Soot has a major impact on contrail properties and may affect cirrus cloud formation. For cooling effects, only two sources are identified: a reduced methane (CH_4) concentration, due to reactions with NO_x emissions, and reduced sun light, due to sulphate aerosols. Note the low level of scientific understanding (LOSU) attributed to contrail cirrus RF.

Furthermore, the climate impact of the in-flight emissions might differ in the lower stratosphere and in the upper troposphere, mostly because the species residence time is much higher in the stratosphere and due to the differences in the temperature profile of the earth's atmosphere (W shape). Large differences in the species atmospheric residence time exist [Penner et al. 1999, Sausen et al. 2009]. A long atmospheric residence time of a species (e.g. CH_4, CO_2) results in a well-mixed distribution throughout the atmosphere; this means, the effects of the aircraft emissions cannot be distinguished from those emitted by any other source. Species with shorter atmospheric residence times (e.g. H_2O, NO_x, SO_x, and particles) remain concentrated near flight routes, in the northern mid-latitudes, in particular. For these reasons, some emissions can lead to radiative forcing that is regionally generated near the flight routes for some components (e.g. contrails) in contrast to emissions that are globally mixed (e.g. CO_2 and CH_4).

An ideal and complete combustion, occurring when burning a stoichiometric fuel/air mixture, is characterized by CO_2 and water as the only products, besides release of energy. The higher the heating value of a specific aviation fuel, the lower the amounts of CO_2 produced for a given thrust, and the lower the contribution to global warming. In addition, the higher the H/C-ratio, the higher the amount of water released:

$C_xH_y+(1+0.25y)O_2 = xCO_2+0.5yH_2O$ + energy.

Further pollutants, besides CO_2 and water (H_2O), the main oxidation products by far, are formed for all other fuel-air ratios. CO, unburned hydrocarbons (UHC), aromatics including polyaromatic hydrocarbons (PAH), and other precursors of particles and soot among them, if the fuel is burned under excess of fuel (fuel rich). Oxygen rich species such as ketones, peroxides, sulphur containing species (SO_2), and nitrogen oxides (NO_x) are emitted, if the fuel is burned under excess of air (fuel lean).

Usually, the maximum of the flame temperature of a hydrocarbon flame is occurring at slightly fuel rich mixtures. For all other fuel-air ratios, the flame temperature is much lower. The power settings most known are those following the LTO-cycle (landing–takeoff, ICAO). However, this is assumed to be not different when burning an alternative or a synthetic jet fuel.

The principles from aromatics to polyaromatic hydrocarbons (PAH) and soot particles are shown in Figure 4-3; for details see [Böhm et al. 2003, Bockhorn 1994, Hu et al. 2000, Böhm and Braun-Unkhoff 2008, Wang 2011]. It is known that the amount of aromatics in a specific fuel is positively correlated to the emissions of particulates. For example, due to the lack of aromatics in neat alternative jet fuels, a reduced effect on contrail formation and climate impact is envisaged, compared to Jet A-1.

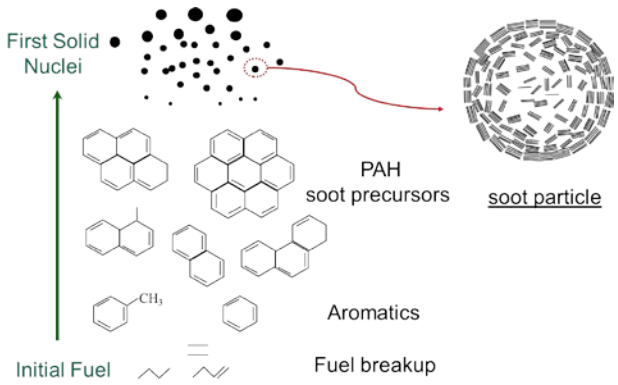


Figure 4-3: Soot formation – principle sketch.

In the past, emissions of PAH from aircraft have been considered to be low, with no need for actions to be taken. However, as pointed out earlier, particulate emissions are in the focus when looking at effects of aircraft emissions on contrails, with the Schmidt-Appleman criterion, to be fulfilled for the formation of contrails, valid for all types of fuels. The main reason is that particles (soot or sulphur containing species) serve as nucleation centres for ice crystal formation, and thus are affecting the number of freshly formed ice crystals. This has an impact on the growth and lifetime of contrails, depending on several meteorological parameters, such as pressure, temperature, turbulence, and relative humidity. Thus, contrails properties may differ if particulate emissions of alternative jet fuels differ compared to those of Jet A-1.

Emissions of alternative jet fuels

Experimental investigations have been performed focusing on the emission pattern of combustors and turbine engines operated with alternative jet fuels, mostly SPK-fuels

(GtL, BtL, CtL), and HEFA. Quite recently, the latest approved alternative fuel component - Farnesane (SIP-fuel) - was also investigated. Studies on emission patterns in exhaust plumes are limited. The fuels were studied both neat and in blends with petroleum-derived fuels [ALFA-BIRD 2007-2013, Altaher et al. 2014, Anderson et al. 2011, Bhagwan et al. 2014, Blakey et al. 2011, Bulzan et al. 2010, burn-FAIR 2011, SWAFEA 2011, Cain et al. 2013, Christie et al. 2012, DeWitt et al. 2008, ECLIF 2015, Li et al. 2013, Lobo et al. 2012, Moore et al. 2015, Moses 2008, Rahmes et al. 2014, Saffaripour et al. 2014, Saffaripour et al. 2011, Snijders et al. 2011, Timko et al., 2015, Wahl et al., 2014, Wahl et al., 2012, Wahl et al. 2011, Zschocke et al. 2015], as a response to the approval protocol. An overview of major relevant studies is given in Braun-Unkhoff and Riedel (2015).

In the studies, the emissions measured include gaseous emissions, mostly CO, CO_2, NO_X, UHC, and particle emissions including mass, number, and size, besides sulphur containing species, aromatics, and aldehydes [Altaher et al. 2014]. For comparison, emission patterns of crude-oil kerosene were measured also. In addition, further parameters such as humidity and temperature as well as physical properties such as viscosity or mean Sauter diameter were also part in some of the studies. Similar, thrust as well as combustor pressure was varied, in order to get further insights into their effect on emissions.

In summary, the evaluations have shown that the emission pattern of alternative aviation fuels show a different picture compared to the one of Jet A-1: Major gaseous emissions (CO, CO_2, and UHC) were reduced slightly, depending on thrust; particulate matter (PM) emissions were significantly reduced (both in mass and particle number); considering NO_x, no clear trend is reported, although mostly reported to be reduced.

CO_2 emissions

The CO_2 emission patterns of crude-oil kerosene and of synthetic kerosene(s) are reported to be almost identical. The negative correlation of CO_2 level with the fuel's energy content was pointed out [Blakey et al. 2011]. Synthetic fuels have a slightly higher calorific value compared to Jet A-1 [Braun-Unkhoff and Riedel 2015, ALFA-BIRD, SWAFEA]. Although these differences are quite low, usually between 1 and 2%, significant lower CO_2 emissions are resulting. This was also shown on engine demonstration flights [Rahmes et al. 2009].

NO_x emissions

Overall, a reduction of NO_x emissions resulting from synthesized aviation fuels was observed. For example, Blakey et al. reported on a reduction by up to 12%, for a FT- or a HEFA-fuel as well as for FAME. For the Alfa-BIRD fuels, differences in the NO_x formation behaviour were measured, with CtL having lower values than Jet A-1, and GtL having the highest values, respectively [Bhagwan et al. 2014]. This behaviour was attributed to their probable different degrees of mixing with air in the combustor. By taking this effect into account, the tendency was shown to correlate well with their different measured combustor temperatures, with GtL showing the highest temperature.

A reduction in NO_x levels was also found in the AAFEX test campaigns, in particular at high power settings, for CtL and GtL fuels [Bulzan et al. 2010, Anderson et al. 2011, Moore et al. 2015]. This finding was also reported for mixtures with GtL as alternative aviation fuels [Wahl et al. 2013, Snijders et al. 2011]. However, the effect was dependent on the type of Jet A-1 used for reference.

With respect to the two farnesane blends, a reduction of NO_x concentrations was observed for most power settings. However, the effect is weak and not completely consistent (cruise) [Zschocke et al. 2015, Wahl et al. 2014].

In addition, it is important to have accurate knowledge on ambient humidity and temperature when evaluating the differences in NO_x emissions between different fuels [Blakey et al. 2011, Bhagwan et al. 2014, Rahmes et al. 2009]. Also, the effect of fuel's physical properties on the correlation of NO_x emissions was discussed [Bhagwan et al. 2014].

Emissions of aromatics, particles, and soot

The measurements performed show a reduction in soot emissions, mostly attributed to the lack of aromatics. Thus, the expected effects of a fuel's chemical composition on its emissions are confirmed; i.e. of aromatics on emissions of soot. Most data were gathered from lab and engine ground tests; data from emissions measured in exhaust plumes are limited.

A clear ranking of the alternative fuels considered in the Alfa-BIRD project with respect to soot concentrations and sooting indices was observed, with the highest values for Jet A-1, and lower values for CtL, GtL + naphthenic cut, GtL, and GtL+hexanol, when measuring soot volume fractions in a laminar diffusion flame at atmospheric pressure [Saffaripour et al. 2011]. Moreover, it was shown that the soot concentrations as well as the threshold soot indices (TSI) values are strongly dependent on the aromatic content of the fuels. In detail, the soot levels in flames were reported to be proportional to benzene concentrations, but not to acetylene levels.

Smoke measurements of the SWAFEA synthetic fuels were performed in an Auxiliary Power Unit (APU) [Blakey et al. 2011, SWAFEA]. Jet A-1 has the highest smoke number, followed by CtL (high aromatic content), and GtL with a very low level of smoke emissions traced back to the near-zero share of aromatics.

However, practically no reduced soot emissions were observed when performing engine ground tests in order to evaluate the impact of alternative fuel blends (HVO) on a V2500 engine, in service on an Airbus A321 [burn-FAIR].

Engine ground tests with two GtL/Jet A-1 mixtures, both of them with a GtL percentage ranging from 10% to 50%, were done on a Cessna Citation II powered with Pratt and Whitney turbofan engines (P&W Canada JT15D-4) [Wahl et al. 2013, Snijders et al. 2011]. The emission indices for particles (mass and number) and particle diameters were reported to be significantly reduced at the power settings used (ICAO LTO points) by increasing the GtL percentage.

A clear improvement was seen in the soot particle emissions when studying the effect of adding farnesane to Jet A-1 [Zschocke et al. 2015, Wahl et al. 2014]. This finding was attributed to the chemical structure of farnesane, being a long-chained iso-alkane. A corresponding reduction in particle emissions was measured when increasing the percentage of farnesane in Jet A 1. A reduction in particle mass was reported at all test points by increasing farnesane content. Furthermore, a reduction of soot surface was measured at all power settings, with a quite clear reduction at high power settings. The number of soot particles has been also reduced, by about 10% to 20%; however, no consistent effect was found on the soot's mean diameter. This finding is of relevance with respect to the adverse health effects of ultrafine particles [Kennedy 2007].

Within the ACCESS measurement campaigns, the impact of jet fuel properties on aerosols emitted by CFM56-2-C1 engines burning 15 different aviation fuels was investigated, with HEFAs and two fossil derived FT-fuels, GtL and CtL, representing synthesized certified aviation fuels [Bulzan et al. 2010, Anderson et al. 2011, Moore et al. 2015]. From the ground test measurements, it was found that the fuel aromatic content, as well as sulphur, has a direct impact on soot emissions for all engine power ranges. The naphthenic content of the fuel determines the magnitude of the soot

number and the soot mass. It is reported that reducing both fuel sulphur content and naphthalenes to near-zero levels would result in roughly a 10-fold decrease in aerosol number emitted per kilogram of fuel burned. In detail, particle emissions from GtL and CtL fuels are substantial lower compared to those of JP-8; e.g. for GtL neat, by about a factor of 20 at low and medium power ranges. Reductions were also observed for GtL/JP-8 blends; however, not proportional. In addition, no soot emissions were measured when using a HRJ-fuel.

Most recently, within the ECLIF flight campaign [ECLIF 2015], particles from the oxidation of several biofuels were also measured. First preliminary analysis of the measured data appear to be in line with the expected results: lower soot levels with lower amount of aromatics in the fuel. In addition, the type of aromatics as well as of cyclic and iso-alkanes were of some influence on the amount of soot particles.

Major combustion properties - ignition delay time (safety) and laminar flame speed (stability)

Safety and reliability are a must with respect to aviation fuels. Two of the most important fundamental combustion properties of any fuel are the laminar flame speed and the ignition delay time. A reliable knowledge of the values for these combustion properties over a relevant parameter range (temperature, pressure, fuel composition, and fuel-air ratio) is therefore of fundamental interest.

The laminar flame speed as a means for describing heat release has a direct impact on the flame length: depending on, the flame will stabilize at different distances from the combustor inlet. For example, if the laminar flame speed of an alternative fuel would differ too much compared to the one of Jet A-1, the heat load of the walls or recirculation zones might change within the combustor. The risk of a flame blowout – also leading to higher levels of pollutants - is increased for low flame speeds at relatively high gas velocities; for high flame speeds, the risk of a flashback exists in premixed systems.

The ignition delay time is an indicator for the stability of combustion. The knowledge on ignition delay times allows a better estimation of the risk of flashback or auto-ignition occurrence. Very low ignition delay times increase the risk of a flashback in a premixed system. With very high ignition delay times, ignition or re-igniting of the fuel might be impossible; in addition, unburned gas might exit the hot reaction zone resulting in an increased amount of unburned hydrocarbons (UHC) in the exhaust gas.

For providing the required knowledge on the combustion properties, sophisticated experiments need to be carried out, within a broad parameter range, e.g. performed in a shock tube (ignition), or in a flame or a bomb reactor (flame speed), although the high demand in time, costs, and personnel is challenging.

Ignition delay times of alternative aviation fuels are reported to be quite similar with those of Jet A-1/A, within the limited parameter range studied. Despite of this, differences in the ignition delay time data are notable, e.g. up to a factor of 2 longer for some of the alternative fuels depending on temperature. Nearly all data were performed by applying the shock tube technique making it inevitable to study the ignition behaviour of the fuels at temperatures almost higher than about 900 K. Data in the NTC (negative temperature coefficient) regime characterized by a quasi-independence of the ignition delay time values with temperature are almost not available. In addition, only a few fuel-air ratios and pressures are considered, with no complete match with respect to the existing fuel-air mixtures range existing in the turbine combustor.

Laminar flame speed data of alternative aviation fuels are reported to be similar with those of Jet A-1, within the limited parameter range studied, mostly at atmospheric pressure, with a few data available at slightly higher pressures. Although

measurements were done by applying different methods, the overall picture is coherent. Differences in laminar flame speed data are notable, in particular in the fuel-rich regime where formation of soot precursors and particles is promoted.

Furthermore, some ignition delay time studies as well as of laminar flame speeds of single components of aviation fuels and of so called model fuels (ignition delay time only) consisting of a few components mimicking a certified aviation jet fuel were also performed. These studies provided some insight into the contribution of molecules from different chemical families on the target observable. For example, concerning ignition delay time, the importance of the n-alkane sub-model was demonstrated [Dagaut et al. 2014]. With respect to laminar flame speed data, large differences are seen depending on the kind of molecule studied (carbon length) and the classification (chemical family).

Species profiles are needed in order to obtain a profound understanding of formation, and destruction pathways as well, of pollutants. Thus, valuable information is provided on how a special molecule as part of a synthetic aviation fuel may contribute to the level of a particular pollutant.

Investigations on the chemical structure of alternative aviation fuels described are mostly performed in jet stirred reactors, both at atmospheric and elevated pressures (10 bar), for selected fuel-air ratios. Information in kind of mole fraction profiles of reactants, several intermediates, and major products are reported. However, for stable species only, neither for radicals which are driving a fuel's oxidation due to their high reactivity, nor for resonantly stabilized species considered to play a dominant role in the formation of particles and soot in particular.

A few investigations of jet fuels were reported in premixed flames. These studies offer the simultaneous detection of many species including radicals; however, only at low pressures (mbar), due to the limited spatial resolution. In addition, experiments were done in single pulse shock tubes, a technique that allows studying the fuel's oxidation at high temperatures and high pressures, over a wide range of fuel-air ratio. Depending on the kind of detection method applied, stable molecules were observed.

5. Development of theoretical emission model, plus variability assessment

5.1. Identification of a global model needed to account for the overall process addressing fuel's performance

Investigating individual sub-processes as described in Chapter 4 is necessary but not sufficient to complete the analysis of fuel's performance. The thermo-physical properties, which govern fuel placement (see Table 4.1), and additionally the combustion properties, which together with the thermophysical properties govern combustor performance and emissions (see Table 4.1) are strongly coupled. The resulting combustion process is extremely complex. Moreover, all these coupled sub-processes occur in a highly turbulent flow, where air and fuel mix under operating conditions which have to cover the entire flight envelope.

A global approach is inevitable if one wants to account for all these sub-processes in realistic geometries under operating conditions relevant to aero-engines. This approach affords the development of several sub-models such as a combustion model, models for describing fuel placement for single and multi-component mixtures, a model for the turbulence-chemistry interaction. These sub-models are then implemented into a unique platform for performing the numerical simulation (e.g. CFD) of the combustion process. Once validated using the few observables accessible to the current diagnostics methods, the numerical simulation gives access to all the variables and parameters describing this complex system. At this stage one should emphasize the necessity to develop models which are able to study the coupling between physical (fuel placement) and chemical (combustion, emission) effects, for fossil based and alternative fuels (Le Clercq et al. 2010).

In addition, the models' requirements and appropriateness need to be revisited with respect to their prediction capability and accurateness for such multi-component mixtures (jet fuels). For example, concerning a reaction mechanism, the number of species (and reactions) needs to meet the CFD code's requirements. This usually affords the construction of reduced kinetic models based on validated detailed chemical kinetic reaction mechanisms.

5.2. Requirements for Empirical Emission Calculation Methods

Global air traffic emission inventories prefer simplified emission models, which are based on a reduced amount of input parameters. Emissions of e.g. NO_X, CO, HC can be derived from aircraft or engine performance simulation models. However, the usability has to be balanced against the accuracy of the emission model results.

Emission calculation models can be divided into two categories: proportional to fuel burn and non-proportional to fuel burn. Emissions of carbon dioxide (CO_2), water vapour (H_2O) and sulphur oxides (SO_X) can be assumed to be proportional to fuel burn, since their emission index can be derived from the carbon, hydrogen and sulphur content of the fuel respectively. Thus, their representation in theoretical emission models is simple and does not change with the fuel type.

Other emissions, like soot particle emissions also referred to as black carbon cannot be assumed to be proportional to fuel burn only. The formation process is complex and influenced by various engine parameters. Figure 5-1 shows an overview on methods to compute in-flight emissions from aircraft engines [Schaefer and Bartosch 2013].

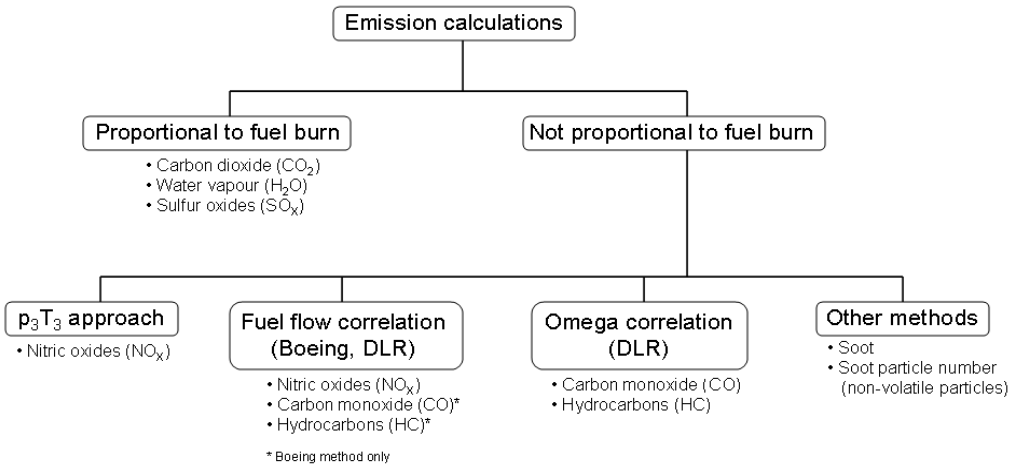


Figure 5-1: Overview of in-flight emission computation methods.

At this point in time, no measured nvPM emissions data from aircraft engines is publically available to base empirical correlation methods on. In the coming years it is expected that such data will be acquired and published in the frame of the ICAO standard setting process, aiming to create a new nvPM mass and number standard for aviation. Therefore, to account for aircraft engine Particulate Matter (PM) emissions, only approximation methods are available today. Four emission models are currently available which are presented and discussed in the following.

5.2.1. FOA3 method

Up to now, ICAO has no certification standard for aircraft PM emissions. However with increasing concern over potential hazardous health effects of fine particles emitted by aircraft engines the member states have decided to task ICAO with the development of an aircraft engine nvPM emissions certification standard. Until this standard is finalized and in force, an interim First Order Approximation method (FOA 3.0) was proposed to estimate total aircraft PM emission in the vicinity of airports. This method is based on the Smoke Number (SN) standard, which was originally introduced to suppress the visible soot trails behind aircraft, as were common in the early days of jet engines. The Smoke Number is measured as the reflectivity reduction of a paper filter after a predefined amount of engine exhaust gas passed through it.

The estimation of nvPM by the FOA3 method is based on the Smoke Number (SN), which is published in the ICAO data base [ICAO 2015] for any commercial jet engine in service, the Air to Fuel Ratio (AFR) and, where applicable, By-Pass Ratio (BPR) of the aircraft engine under consideration. In a first step, the Smoke Number is converted into a Carbon Index (CI) by an empirical correlation:

SN ≤ 30: $$CI = 0.06949 \cdot SN^{1.234} \quad [\frac{mg}{m^3}]$$

SN > 30: $$CI = 0.0297 \cdot SN^2 - 1.803 \cdot SN + 31.94 \quad [\frac{mg}{m^3}]$$

The Carbon Index gives the nvPM mass per unit volume of exhaust gas. The Emission Index (EI) is then calculated by multiplying the volume flow of exhaust per kilogram of fuel, Q. Q is calculated as a function of the engine AFR and, if the SN was measured in the exhaust of a mixed flow engine, the BPR. The AFR is not given in the ICAO engine emissions data base, therefore the following representative AFR values should be used for the individual engine power settings:

Table 5-1: Engine power settings and corresponding air-fuel ratios

Engine Power Setting [% F_{00}]	Representative AFR [-]
7% (Idle)	106
30% (Approach)	83
85% (Climb-out)	51
100% (Take-off)	45

For SN values, measured in the engine core flow, the volumetric flow rate at standard pressure and temperature is calculated by:

$$Q_{Core} = 0.776 \cdot AFR + 0.877 \quad [\frac{m^3}{kg}]$$

and for SN values, measured in the exhaust of a mixed flow engine:

$$Q_{mixed} = 0.7769 \cdot AFR \cdot (1 + BPR) + 0.877 \quad [\frac{m^3}{kg}]$$

Finally, the emission index of non-volatile particulate matter for each engine power setting is calculated by

$$EI_{nvPM} = CI \cdot Q \quad [\frac{mg}{kg\ Fuel}]$$

For the complete calculation procedure including example calculations and further equations for volatile organic and sulfur particles see [ICAO 2011].

The FOA3 methodology is applicable to calculate sea level static PM emissions data only. The accuracy of the FOA3 results is by nature limited by the accuracy of the underlying Smoke Number and AFR data. The generic AFR data as given in Table 5-1 were agreed with engine manufacturers and should not be replaced by data from other sources, e.g. from an engine performance program, because -although such data might reflect actual engine conditions more realistically — the correlations used by the FOA3 method were tailored around these generic AFR values and their applicability with other values has not been verified.

Furthermore it is well known that measured SN values can vary by as much as ±3 SN [ICAO 2008]. Additional to this inaccuracy, the permeability of the paper filter used for the SN measurements might be different for different particle sizes. This was analyzed and discussed in detail by Stettler et al. [Stettler 2013b]. As a result of the analysis it was found that the FOA3 correlations are valid only for particles with a Geometric Mean Diameter of around 60 nm. For smaller particles the correlations were found to significantly under predict particle concentrations.

Since non-volatile exhaust particles of modern engines are more in a size range of 20-30 nm, where the standard FOA3 correlations may give too low particle concentrations, the following alternative correlation was proposed [Stettler 2013b]:

$$C_{BC} = 0.236 \cdot SN^{1.126} \left[\frac{\mathrm{mg}}{\mathrm{m}^3}\right]$$

The results of the method using this correlation could demonstrate better agreement with latest available measurement data than the original FAO3 correlation.

5.2.2. FOX method

To overcome the inaccuracies coupled with the Smoke Number to concentration conversion, an alternative method has been proposed in [Stettler 2013b], which is not based on SN data but uses available PM measurement data from various campaigns.

The correlation formula for calculating the black carbon concentration CBC in the engine exhaust is based on Arrhenius models for soot formation and oxidation:

$$C_{BC} = \dot{m}_F \cdot \left(A_{Form} \cdot e^{\left(\frac{6390}{T_{Fl}}\right)} - AFR \cdot A_{Ox} \cdot e^{\left(\frac{19778}{T_{Fl}}\right)} \right) \left[\frac{\mathrm{mg}}{\mathrm{m}^3}\right]$$

where the factors A_{Form} and A_{Ox} need to be calibrated for each engine type individually with measured data. Flame temperature T_{Fl}, fuel flow m_F and AFR may be calculated with an appropriate engine performance program. With the AFR available the black carbon concentration is easily transformed into an Emissions Index, EI_{BC} [mg/kg].

The authors claim that with this method more accurate estimates of black carbon emissions are possible at ground and even cruise conditions. However the method is applicable only if sufficient measurement data is available. Moreover the resulting exhaust concentration is calculated by subtracting two large, nearly equal numbers which is prone to a numerical problem known as loss of significance. This may cause large inaccuracies for operating conditions which are not close to those used to calibrate the formation and oxidation factors.

5.2.3. DLR nvPM calculation method

In a conventional jet engine combustor a large number of soot particles is formed in the combustion primary zone, most of which are subsequently oxidized in the following regions of the combustor. The remaining particle concentration at the combustor exhaust is several orders of magnitude lower than the peak concentration. Modelling these two processes individually leads to a loss of significance in the final result, because the exhaust concentration is obtained by subtracting two large, nearly equal numbers. To overcome this numerical problem, the DLR soot correlation is based on the assumption that the PM emission characteristic of a given combustion system can be defined for all operating conditions as a function of characteristic parameters of the respective engine type. This emission characteristic is defined as a so-called variable reference function, which means that it is derived for each engine type individually, usually on the basis of measured sea level static reference data. The method is suitable to calculate nvPM emissions data under any operating condition.

The standard application procedure takes Smoke Number data from the ICAO engine emissions data base [ICAO 2015] as the reference, because this information is available for any commercial jet engine type in service. With these reference data, the Emission Index is calculated by the following three step approach:

- The nvPM concentration C_{nvPM} [mg/m³] is estimated from smoke number measurements at sea level static conditions. Several correlations are available to perform this step, in most cases Several correlations are available to perform this step, in most cases

  SN ≤ 30: $CI = 0.06949 \cdot SN^{1.284}$ $[\frac{mg}{m^3}]$,

  SN > 30: $CI = 0.0297 \cdot SN^2 - 1.803 \cdot SN + 31.94$ $[\frac{mg}{m^3}]$ or

  $C_{BC} = 0.236 \cdot SN^{1.126}$ $[\frac{mg}{m^3}]$

  would appear appropriate.

- A reference function of nvPM concentration versus combustor inlet temperature, $C_{nvPM} = f(T_3)$, is determined for sea level static conditions (separately for each engine type considered).
- Emission indices are calculated from the reference functions using corrections for combustor inlet pressure p_3, flame temperature T_{FI} and equivalence ratio φ.

The formula used for the third and final step is known as the DLR soot correlation:

$$C_{nvPM} = C_{nvPM,Ref} \cdot \left(\frac{\phi}{\phi_{Ref}}\right)^{2.5} \cdot \left(\frac{p_3}{p_{3,Ref}}\right)^{1.35} \cdot \frac{e^{(-20000/T_{FI})}}{e^{(-20000/T_{FI,Ref})}} \quad \left[\frac{mg}{m^3}\right]$$

Flame temperature T_{FI}, combustor inlet pressure p_3 and equivalence ratio φ may be calculated with an appropriate engine performance program. With the φ available the black carbon concentration is easily transformed into an Emissions Index, EI_{BC} [mg/kg]. A detailed description of the method is found in [Döpelheuer 2001] and [Döpelheuer 2002].

The DLR soot calculation method also includes a calculation procedure for particle number. Current state of knowledge concerning the number of soot particles emitted by aircraft engines must be considered as low. Very few detailed measurements of particle size distributions are available. From an analysis in [Döpelheuer 2002], an average characteristic of specific particle number vs. altitude was developed and is shown in Figure 5-2.

Given the emission index (EI) of soot in gram per kilogram and an estimation of the average particle number per gram soot from Figure 5-2, the particle number emission index (PEI) can be calculated as follows:

$$PEI_{Soot} = EI_{Soot} \cdot N_{Soot}$$

where: PEI_{Soot} = Soot particle number emission index in [1/kg]

EI_{Soot} = Soot emission index in [g/kg]

N_{Soot} = Average particle number per gram of soot in [1/g]

It should be noted that the accuracy of the method for particle number calculation is unknown and probably low. As a consequence, results obtained by using the method described above should be regarded as rough estimates only.

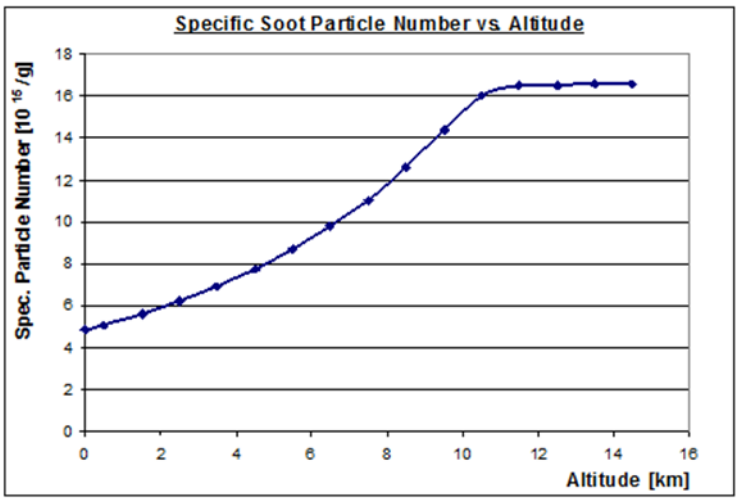


Figure 5-2: Specific soot particle number as a function of altitude.

Due to the reference function, which is individually created for each engine type to be modelled, the DLR nvPM calculation method is more flexible than the other methods described above. As can be seen from the Smoke Number data in the ICAO data base, the emission characteristics of different types of engine, especially from different manufacturers, vary significantly in magnitude as well as curve shape. When applying the DLR method, the use of an appropriate reference function might be sufficient to cover these variations. In comparisons with the few available PM measurement data, the method could demonstrate satisfactory accuracy [Döpelheuer 2002]. However, the best possible accuracy can only be achieved with a high quality engine performance model and appropriate reference data. The use of smoke number data, converted to PM concentration by one of the correlations given in this report, might be a major source of inaccuracies in the application of this method, due to the inherent inaccuracies of these data and correlations.

5.2.4. ASAF Formulation

Speth et al. (2015) provide a formulation to estimate black carbon emissions for alternative fuels. They propose a relationship between fuel aromatic content, thrust setting and BC emissions. The formulation is derived from a simple theoretical concept of soot formation and has only one adjustable parameter, λ, that is fixed by fitting the predictions of the formulation to results from recent measurement campaigns listed in tables 1 and 2 of the paper. The theoretical concept of soot formation is that of formation, growth and oxidation of polycyclic aromatic hydrocarbons (PAH). If aromatics are already present in the fuel, the rate of PAH and soot formation depends on the rate at which aromatic molecules are transported into a region in the combustion flame where the so-called HACA mechanism can proceed. The rate of PAH formation is then modelled as the sum of a component that only depends on the thrust and a component that also depends on the aromatic content of the fuel. The resulting formulation uses normalised quantities B/B_{std}, F/F_0, and $\hat{A}$, that is BC emission rate divided by the BC emission rate when standard kerosene is burnt, rated thrust, that is, actual thrust setting, F, divided by full thrust, F_0, and aromatic content divided by the average aromatic content of kerosene. The so-called ASAF (Approximation for Soot from Alternative Fuels) formulation is:

$$B/B_{std} = \lambda(F/F_0) + \hat{A} - \lambda(F/F_0)\hat{A}.$$

λ ($0 \leq \lambda \leq 1$) is a fit parameter. It can be interpreted in two ways. For a fuel without aromatics ($\hat{A}=0$) it describes the rate at which the first aromatic rings are formed in the fuel, which is modelled as proportional to thrust setting ($B/B_{std} = \lambda(F/F_0)$ in this case). Otherwise ($\hat{A}>0$) it describes how sensitive BC emissions depend on thrust setting. The range of BC emission rates between zero and full thrust increases with the value of λ (see Figure 5-3).

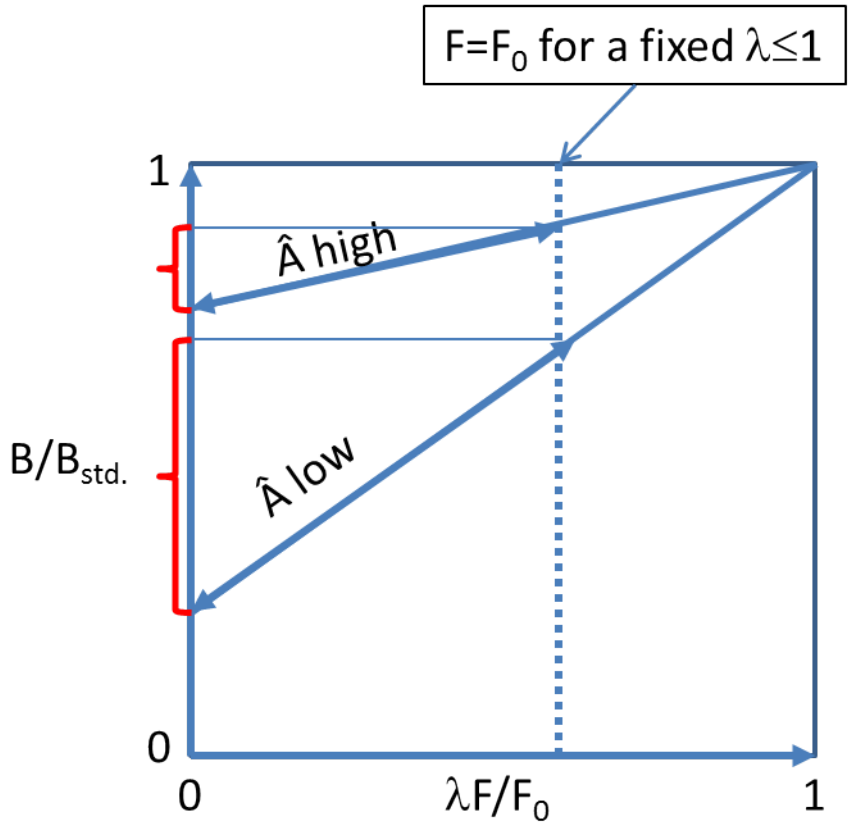


Figure 5-3: Emission of Black Carbon from a biofuel relative to that of kerosene (B/B_{std}) as a function of rated thrust (F/F_0, i.e. thrust divided by maximum thrust) for alternative fuels with different aromatic contents (normalized to the average aromatic content of kerosene, Â). The value of λ ($0 \le \lambda \le 1$) describes how sensitive BC emission depends on thrust setting. The broken vertical line marks full thrust for a fixed value of $\lambda < 1$. Read braces on the lhs axis indicate the range of BC emission between no thrust and full thrust.

The ASAF formulation of Speth et al. is valid for FT and HEFA alternative fuels, but may also be valid for other paraffinic alternative fuels. It distinguishes between emissions by number and mass, using

λ_N=0.37 (0.32-0.43, R^2=0.72), λ_M=0.25 (0.17-0.32, R^2=0.56).

Values in brackets are 95% confidence intervals and R^2 is the squared correlation coefficient between the measurement data and the corresponding ASAF prediction.

The fact that $\lambda N > \lambda M$ shows that with increasing thrust setting number emission rates increase faster than mass emission rates. This is consistent with the observation from measurements (e.g. AAFEX, Bulzan et al. 2010) that soot particles resulting from alternative fuels are smaller than those from kerosene. Indeed, a normalised diameter $D/D_{std} = (\lambda_M/\lambda_N)^{1/3} \approx 0.88$ can be derived which agrees very well with data from the AAFEX campaign.

Moore et al (2015) use results from APEX, AAFEX (I and II) and ACCESS-I to derive multilinear regression formulae that relate emission indices (mass and number based) for volatile and non-volatile (i.e. mainly soot) particulate emissions to fuel composition (sulphur, aromatics and naphthalene contents) and ambient temperature. The regression coefficients have been derived for settings 4, 7, 30, 65, 85, and 100% power. The squared correlation coefficients are typically around 0.6 or even higher

except at the very low power setting of 4% which is however irrelevant to the consideration of contrails.

5.2.5. Linear regression model

For the determination of significant fuel properties and quantification of the emissions impacts Moore et al (2015) evaluated aerosol emission data sets from the APEX, AAFEX (I and II) and ACCESS-I measurement campaigns comprising 15 different aviation fuels and blends. A simple multiple linear regression model was derived for the settings of 4, 7, 30, 65, 85, and 100% power at sea level static conditions using the engine fuel flow rate as the primary quantitative metric. The analysis emphasises the importance of the sulphur, aromatics and naphthalene contents for volatile and non-volatile (black carbon) particulate emissions in terms of mass and number emission index, also taken the ambient temperature into account. Although the squared correlation coefficients are typically around 0.6 or even higher (except at the very low power setting of 4% which is however irrelevant to the consideration of contrails) the considered emission data sets are correlated solely to the CFM56-2-C1 engines, powering the NASA Douglas DC-8 research aircraft. It can be expected that the derived correlations and relationship between emission indices and fuel flow rate would alter using different engine types.

5.2.6. Additional influence factors on emissions and uncertainties

There are obviously much more influences on soot (BC) formation than accounted for in the simple emission models. In preparation of the AAFEX experiments the BC emission indices from burning the same fuel differed by factors exceeding two in the exhausts from two engines of same type, same age and same maintenance and servicing (the two inboard engines of the test aircraft, Beyersdorf et al. 2014). Much larger variations for the same fuel type must be expected for engines of different types, age and maintenance. Beyersdorf et al. thus compared their results of soot emission reductions with results obtained in another experiment by Timko et al. (2010) who used the same type of kerosene (JP-8), but another engine type (PW308 vs. CFM-56). Reductions of $EI_{soot,N}$ and $EI_{soot,M}$ (EI_N and EI_{BC} in the original paper) of Fisher-Tropsch fuels and 50/50 blends relative to JP-8 over the whole range of thrust (idle to take-off power) have been compared. At idle power both experiments gave 80% reductions for 50/50 blends. But reductions decreased with increasing power setting to different degrees. At 85% power, reductions while using the blends were still quite large in the AAFEX experiment, but no reductions were found by Timko et al. under these conditions. The emission reduction for the neat FT fuels was much larger in AAFEX than in Timko's experiments.

For more detailed emission predictions, enhanced methods have to be developed, taking fuel kinetic and combustion physics, and CFD simulation methods into account. This leads in turn to a much more complex setup and a larger number of input parameters, which require significant effort to obtain and e.g. are not feasible for global emission inventories.

5.2.7. Requirements for the development of a future emission model

The aforementioned emission models do have their specific assets and drawbacks. In general one can conclude that these methods either focus rather on the impact of engine characteristics or rather on the impact of fuel characteristics.

For the development of a novel theoretical emission model for alternative fuels, both aspects have to be considered concurrently. Therefore it is recommended to correlate the nvPM emission with characteristic engine parameters to account for the engine

performance and with characteristic fuel properties to consider different fuel type and blend ratios.

In terms of engine performance, the models emphasise that the emissions of non-volatile particulate matter depend on the engine power setting and the current engine design and technology level. Characteristic performance parameters, e.g. like combustor inlet temperature and/or pressure and the fuel flow rate or AFR may be a good indicators to reflect the engine performance. Furthermore these parameters may be suitable to predict cruise level emissions based on SLS test data. A calibration with SLS test data is required to account for the specific engine configuration and combustor technology level, e.g. like staged combustion.

Characteristic fuel properties should consist of the most significant impacts on nvPM emissions, e.g. like aromatic content and the nature of the aromatic species. Consequently, the carbon-to-hydrogen ratio or the hydrogen-content of the fuel may be favourable, since the hydrogen-content is affected by the aromatic content and the aromatic species. Moreover, fuel sulphur content may be important as well for the effectiveness of nvPM emissions and as nuclei for the formation of ice crystals.

However, to develop such an emission model, high quality test data and a sufficient database is required to derive appropriate correlations. It has to be considered that line losses may impose potential inaccuracies to the measured nvPM data. Finally, the prediction of particle number seems to be a function of the ambient conditions and therefore of flight altitude and may not be as accurate as the nvPM mass concentration prediction.

6. Proposals for practical test set-up to validate model

For the validation of the emission model, a multi-level analysis and hence practical test set-up is recommended to cover all relevant aspects of emission formation and to unravel its complexity. Each level is focused on different drivers and enables the application of diverse measurement techniques and variation of boundary conditions. The following proposal for practical test set-up comprises the full range from subscale burner experiments, CFD simulations up to full scale combustor rig experiments. For the fuel of interest, the first step is an analysis of its major physical properties and the chemical structure – qualitatively and quantitatively, identifying the molecules including their carbon length, structure, chemical family as well as their energy content.

6.1. Experiments needed for validation of the models describing fuel placement and combustion - for biofuel and kerosene/biofuel blends

Aviation jet fuels certified to date are composed of a variety of many hydrocarbons, with a large variation in percentage and type of hydrocarbons, also with respect to the kind of chemical families. The fuel's performance including emission pattern is determined by its chemical nature, i.e. the thermophysical and thermochemical properties of the fuel's components (composition), affecting also its suitability with respect to safety issues.

In order to be able to interpret the emission pattern of a jet fuel and to predict as well, when burning a jet fuel in the combustion chamber, the relevant processes need to be understood and described comprehensively. Within this context, the fuel and combustion system related parameters have been identified (Figure 3-1), with fuel's placement and fuel's combustion playing a pivotal role.

The processes identified must be investigated for each of the alternative fuels of interest, for the relevant range of parameter. Due to the large variation in the composition of a jet fuel, major challenges exist in three points: (i) in the fuel's complexity; (ii) in the parameter range to be covered; (iii) in the fuel's amount required for the measurements.

To rely on experiments solely implies some shortcomings. They are mostly highly time- and cost extensive. In addition, it may happen that not the entire bundle of measurements can be performed to study the influence and effect of a particular property, although highly desirable, e.g. in case the fuel is not available, or for parameters which may not be experimentally accessible.

This suggests the deployment of numerical models that allow to describe the thermo-physical and thermochemical properties of a fuel as well as the detailed processes occurring during the fuel's placement (dominated by thermo-physical properties) and the fuel's combustion (dominated by chemical properties) (see Figure 6-1).

For exploiting the potential of numerical models serving as a virtual fuel performance test rig, the validation of each of the models by relevant experiments is essential, for a reliable and accurate calculation of the target values, e.g. the influence of selected parameters on the fuel's emission, or the evaluation of the global significance of fuel's emission data obtained when burning the fuel in a particular combustion engine.

Experiments needed for the models` validation are identified considering experiments to be performed at atmospheric pressure and high pressures as well, in a lab test rig, under well-defined initial conditions e.g. using a generic spray burner or a shock tube, or a gas turbine test rig.

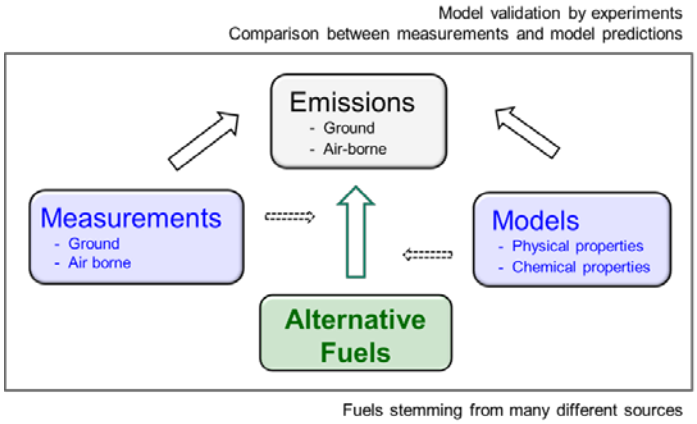


Figure 6-1: Strategy how to study effects of composition of different aviation fuels on fuels emissions.

6.1.1. Experiments needed for validation of the models describing fuel dependent sub-processes - for biofuel and kerosene / biofuel blends

A validation experiment needs to focus on a very limited number of sub-processes; actually the ideal case would be one sub-process per experiment. Then, the metrological tools and diagnostics methods should definitely enable to measure quantitatively fuel composition dependent observables. As the fuel composition dependency is sometimes difficult to isolate it is here also very important to define all the boundary conditions very accurately. In other words, looking at the phenomena under investigation is important (e.g. flame properties) and defining the proper sensors and controllers for the rig is as important, as it enables to set accurate boundary conditions.

A systematic issue when developing experiments at the engine-component level is related to the intellectual property (IP). Actually, technological details such as component geometry or materials are patented and the key observables and thermodynamic characteristics (e.g. temperature, pressure, etc.) are strictly confidential. Consequently, in terms of defining experiments dedicated to model validation, one should focus on generic components under relevant conditions in order to avoid these IP issues. The sub-processes listed below are identified as being fuel composition dependent. They are all relevant for the alternative aviation fuel approval process and have a direct or indirect effect on emissions. Direct in the sense that spray characteristics, for example, are directly related to how good the air and fuel mix in the combustor, which affects directly pollutant emissions. Indirect in the sense that introducing a rich pilot stage in a combustor chamber to guarantee safe operations (flammability limits: ignition and LBO within safe range) increases emissions. In the list below, the complexity is gradual as each sub-process depends also on the ones listed before. For example, spray ignition depends on how the flame propagates in a multiphase flow, how the fuel evaporates and obviously, on the fuel particles position, size and velocity distribution (e.g. outcome of atomization process).

- Atomization (Eckel et al. 2013). There are different kinds of injectors, for instance jet-in-crossflow atomizer, pressure swirl atomizer, airblast atomizers. Each displays a different sensitivity to the liquid fuel properties. Although the number of physical properties which affect the atomization process (see Table 4-1 in chapter 4) is relatively small compared to other processes, currently, there are as many empirical correlations as injector types and no fundamental and generic model which would predict the spray characteristics for each type of atomizer. The consequence is that at least each family of atomizer should be tested for its dependency upon fuel

composition and that generic rigs should be developed to investigate this dependency. One could argue that such tests are performed by OEMs on a daily basis but the IP issues restrict the access to the results. Generic experiments performed with commercially available injectors would generate the database necessary for validation purposes.

- Evaporation (Rauch et al 2011). To separate this physical sub-process from the previous one, one should use a well characterized injector and generate a spray in a well characterized hot turbulent flow. The difficulty here is not so much on the droplet sizing but more on the fuel vapour composition. Jet fuel under engine-like conditions does not follow the classical distillation curve. The objective is to identify the chemical species which evaporate first and thus contribute to the ignition for instance and which species evaporate later and would be candidates for specific emission pathways.
- Flame propagation in a multiphase flow (spray) (Neophytou and Mastorakos 2009, Boyde et al. 2013). The objective of this generic experiment would be to investigate the coupled influence of fuel evaporation and reactivity (kinetics). There are already dedicated experiments to look at the flame speed (in gaseous environment) or to look at the fuel evaporation. There is no linear dependency when both processes are coupled thus it is necessary to investigate such flames and generate a proper database with single component as well as multicomponent-fuels for model validation. The speed at which the flame front propagates in a well-defined multiphase flow, for instance a monodisperse stream of droplets, shows a fuel composition dependency.
- Spray ignition (Boyde et al. 2013). Under normal conditions (sea level start), under cold conditions (sea level cold start) and under high altitude relight conditions. The issue of igniting the engine, especially under adverse conditions, has re-arisen, due to the shift of the combustion chamber design to leaner conditions to fulfil policy requirements of pollutant emission and due to the introduction of alternative fuels. The first phase of spray ignition is the generation of a flame kernel. This is not considered to be fuel dependent. However, the flame propagation (see bullet point above) and the stabilization of the flame in the primary zone, which are phase 2 and phase 3 (Lefebvre 1983) of spray ignition, respectively, are considered fuel composition dependent.
- Combustion system stability and lean blowout. Stringent emission norms require gas turbines to operate with extremely low NO_x emissions. Lean combustion systems (low NO_x system) are thus under development. However, they are extremely susceptible to thermoacoustic instabilities (see bullet point below) and lean blowout (LBO). As power and fuel flow decrease, the combustor flame is susceptible to extinguish via blowout, in which the flow rates in the combustor are too rapid to allow the flame to stabilize. It is currently not completely clear whether this is related only to the fuel kinetics or to the fuel physical properties and spray characteristics or to both. However, it is certainly fuel dependent. For safety reasons the lean blowout limits need to be defined for each combustor and each approved fuel. As this is at the core of the modern lean combustion systems development, the geometries are proprietary. Thus, the difficulty here resides in defining a generic rig, which would guarantee that if a fuel composition displays changes in the LBO limits these changes would be similar in the proprietary geometry.

6.1.2. Experiments needed for validation of the models describing combustion - for biofuel and kerosene / biofuel blends

The complexities in a jet fuel in conjunction with the wide parameter range when burning in a jet engine, under turbulent conditions and at high altitude, are the major

challenges in achieving a comprehensive understanding and description of the emission pattern of the fuel of interest.

Therefore, the idea of so-called surrogates or model fuels is used to describe the combustion of kerosene. A surrogate is composed of several hydrocarbons selected from those chemical families which represent the major components and their fraction in the fuel of interest [Dagaut and Cathonnet 2006, Steil et al. 2008, Braun-Unkhoff and Riedel 2015]. The interconnection between these hydrocarbons is described by elementary reactions, which as a whole are forming the so-called detailed chemical kinetic reaction model. A surrogate can be built such that it will have physical and chemical properties similar to those of the real jet fuel. To date, several formulas for a surrogate exist, consisting of about one digit number of hydrocarbons depending on the objective.

Such model fuels are of high interest because they allow studying the effect of chemical composition on the fuel's properties and on the combustion process [Kick et al. 2011, Kick et al. 2012, Mzé Ahmed at al. 2012, Dagaut et al. 2014], once a reaction model exists that was validated by measurements covering the whole range of experimental parameters needed. Thus, it is ensured that the combustion process and the emission pattern can be studied in detail, for a specific question, e.g. effect of a specific aromatic molecule on the amount of soot particles, within the whole parameter range.

In addition, such reaction models are a precondition for CFD simulations to predict the emission pattern of the fuel of interest under real flight conditions, i.e. taking into account the interactions between fuel placement, fuel combustion, and turbulence mimicking the oxidation of a jet fuel in a jet turbine. In summary, the reaction model can be regarded as a virtual fuel, which can be studied by running CFD simulations, serving as a virtual gas turbine test rig (see Figure 6-2).

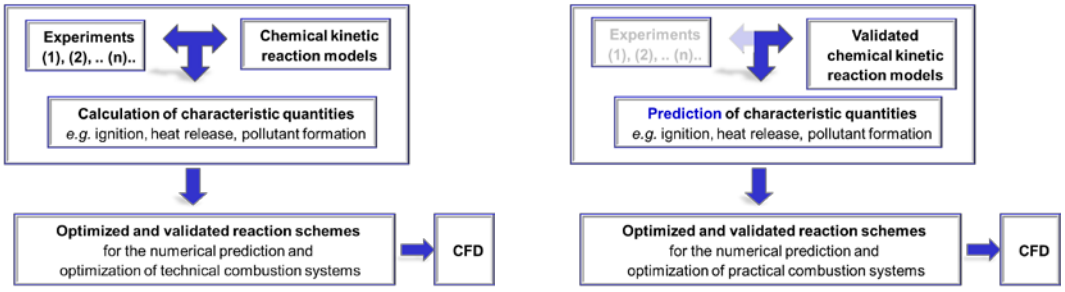


Figure 6-2: Combustion properties of alternative fuels – from experiments over reaction mechanisms validated by experiments to predictions exploiting numerical calculations – Workflow numerical modelling (CFD), as a virtual gas turbine test rig.

For these reasons, validation experiments are identified which are needed with respect to the formulation of a detailed reaction mechanism as part of the combustion model. Measurements of ignition behaviour, as part of the reliability tests, flame speeds, as part of the evaluation of the flame's stabilization, and of reactants, intermediates and products occurring within the fuel's combustion, as part of the fuel's emission pattern, are imperative to describe the oxidation and thus, the emission pattern of the fuel of interest (chapter 4). Knowledge of these properties is essential to guarantee a less harmful impact on the environment, but also to address safety issues (e.g. re-ignition in high altitude; LPP (lean premixed pre-evaporized) concept). Ignition delay time,

laminar flame speed, and species profiles of reactants, intermediates, and products have been identified as the data needed

To allow the study of the effect of a special species on the fuel's performance, experiments must also be performed for key molecules, for each chemical family, and generic mixtures as well.

These experiments must be conducted for a relevant range of temperature, pressure, and fuel air ratio.

Knowledge of these data are of value per se, as part of the evaluation of the technical suitability of a fuel, and when compared to the crude oil based kerosene. In addition, and even more important, this experimental data-base is essential for the construction, further optimization, and validation of a detailed chemical kinetic reaction mechanism.

In terms of a detailed chemical kinetic reaction model able to predict the combustion of a (model) fuel of interest, sophisticated experiments and calculations as well, are indispensable. These studies must be performed very comprehensively in particular for those molecules which are building the model fuel mimicking the fuel's composition. Depending on the specific fuel, the molecules to be selected are belonging to different chemical families, i.e. branched, unbranched, and cyclic alkanes of different carbon size, as well as aromatics. Knowledge is needed for fuel lean, stoichiometric, and fuel rich mixtures, at temperatures and pressures ranging between about 700 and 2200 K, and 1 to 50 bar, respectively. It is clear that several types of experimental approaches have to be exploited. Furthermore, to evaluate the performance of the models developed, a restricted number of experiments are also needed for the model fuel(s) itself as well as of the fuel(s) of interest.

For ignition delay times, data can be gathered e.g. by applying the shock tube technique, rapid compression machines, or bomb reactors. For laminar flame speeds, data can be gathered by different burner experiments or bomb reactors. For species profiles, data can be gathered by different methods equipped with a sophisticated detection technique, e.g. by applying shock tube techniques (single–pulse), plug flow reactor, burners, and jet flow reactors, all of them combined by GC or GC/MS detection methods, some of them may gain from an ionization technique which allows to detect radicals and isomers, in addition. The experiments suggested will give detailed insight into the oxidation pathways of a fuel of interest allowing tracing back the emission pattern to its composition.

However, additional studies, with the help of modern numerical tools, i.e. quantum chemical calculations, are essential, to acquire sound information on the pressure dependence of a specific elementary reaction or the branching ratio, and thus the products, of a specific reaction. Furthermore, as the probability of a reaction is dominated by the energy needed to break-up and, to build-up as well, a chemical bond, the activation energy must be known precisely; however, this can be very tricky due to rotational effects of the species involved in a reaction resulting in an energy barrier. In addition, precise thermochemical data must be available, to describe the dynamics of an elementary reaction, i.e. to account for the chemical equilibrium, dominated by rate coefficients in forward and reverse reactions.

From the combined experimental and theoretical efforts described, a detailed validated reaction model is elaborated, for the (model) fuel(s) of interest. Depending on the observables and the targets, such a model might consist of several hundreds of individual species and thousands of reactions. To enable the numerical simulation in a virtual gas turbine test rig (CFD-calculations) and a detailed description and analysis of further determining factors (thermophysical processes) in an acceptable time

frame, requirements exist to a chemical reaction model, in particular with respect to number of species included.

This requirement is solved by the development of a so-called reduced reaction model starting from a validated detailed reaction model. A reduced reaction model is reduced with respect to number of species and reactions by the analysis of the global combustion of the fuel. Thus, unambiguously needed (important) reactions and species are identified, with respect to the targets observable and parameter range desired.

Several methods exist in developing such a reduced reaction model. The challenge is in the creation of a reduced reaction model that is behaving well when introduced into a CFD code, with an acceptable size in terms of number of species and reactions included and with keeping the grade of quality in predicting the combustion of the fuel of interest.

Following this strategy, the combustion of a fuel can be studied in detail by using a (reduced) reaction model simulating the fuel of interest with the help of CFD simulations serving as a virtual gas turbine test rig to predict the emission pattern under real flight conditions.

6.2. Validation of emission models: rig experiments

6.2.1. Test rig setup

To validate the emission model, practical test data are required. To avoid the high costs of full engine testing, combustor rig tests may be appropriate, because such tests would allow for sufficient variation of combustor operating conditions. Furthermore, the most significant impact parameters on particle formation and oxidation, namely temperature, pressure and fuel to air ratio (FAR) can be varied independently in such tests. The evaluation and validation of the fuel-specific impact of these parameters is crucial for the accuracy of PM emission models.

The test object should be similar to, or typical for, a modern in-service RQL combustor to achieve results that are significant to today's aircraft applications. Preferably a multi-sector combustor segment should be tested, to account for interactions with neighbouring sectors and to reduce effects from the cooled side walls, which are not present in an actual full-ring engine combustor.

In an aircraft engine, the combustor exit flow is rapidly cooled down in the subsequent turbine, which effectively stops the soot oxidation processes. To measure PM emissions on a combustor test rig, measures have to be taken to simulate this process (e.g. by a cooled sampling probe).

6.2.2. Measured data and equipment

The number of particles emitted by an engine is the most important fuel-related impact on contrail formation. Therefore the highest priority should be on measurement of PM number concentration in the combustor rig exhaust for different types of fuels and operating conditions.

PM mass and size distribution measurements could provide further insight into PM properties which impact climate relevant contrail properties (e.g. optical thickness). To provide optimum data quality, the sampling system and measurement equipment for PM number and mass should be compliant with SAE AIR6241 to the extent possible for combustor rig tests. An additional SMPS installation is recommended for size distribution measurements to show (or exclude) potential impacts of different fuels on

contrail properties (due to different primary particle size or potential shifts in the size distribution).

A sampling position at the combustor exit is required to validate the simpler, correlation based modelling approaches, which aim to calculate the net PM production of the combustor. In addition, another sampling position after the combustor primary zone could help to understand the competing production and oxidation processes, which result in that net PM emission rate, and to improve the more detailed, physics-based emission models which account for both of these processes separately.

6.2.3. Measurement program

Measurement program should include independent variation of T, p and FAR for each fuel to be tested, to evaluate individual influence factors (exponents) for these most important impact parameters. These tests should be followed by combined variations of these parameters, representing typical engine operating conditions in cruise (cruise operations are most relevant for climate impact) and ground operations (LTO-cycle data is usually required as base data for cruise PM modelling and is furthermore most relevant for local air quality and health effects). The required combined operating parameters for these test conditions should be provided by a sufficiently accurate engine performance model.

6.3. Validation of emission models: ground and flight tests

Model simulations of jet engine emissions and contrail formation and properties require validation by measurements including ground and flight tests. The purpose of the ground tests is to characterize and quantify the primary emissions and their evolution over a range of power settings when burning different types of fuel (kerosene, biofuels, FT fuels, and blends of alternative fuels with kerosene). The flight tests aim for measurements of emissions and contrails of a jet aircraft at cruise altitudes when burning FT fuel/kerosene and biofuel/kerosene blends in comparison with conventional kerosene.

The general set-up for ground tests include a source aircraft parked in an open-air run-up facility, inlet probes positioned downstream of the aircraft's engines, and sample lines connecting the inlet probes with instrumented vans or containers located on one side of the aircraft. Gas and particle emission measurements are performed for the different test fuels as a function of engine thrust. Pairs of fuels burned in different engines are compared. Conventional kerosene is alternately used in one of the engines or in both to record differences of the two engines. In order to examine plume chemistry and particle evolution in time, the inlet probes may be positioned in different distances to the exit of the engines (e.g. 1, 10, and 30 m). Important engine operating parameters and ambient meteorological data need to be recorded in conjunction to the exhaust sample data. Such a ground test set-up was successfully used during AAFEX (Anderson et al., 2011) and the recent ACCESS2 and ECLIF1 field campaigns.

The general procedure for flight tests includes formation flights of a source aircraft and measurement aircraft in a restricted air space. Due to safety considerations, the measurement aircraft is able to sample the exhaust/condensation trail in the near field of the source aircraft (50-200 m) and at a distance where the wake vortices of the source aircraft have decayed to safe conditions for interception by the measurement aircraft (app. 10 km, dependent on the size and weight of the source aircraft). The measurement altitudes will be selected according to the altitude where the Schmidt-Appleman criterion for contrail formation is fulfilled (altSA). Measurements should be performed a different altitudes above altSA (different temperatures below tSA) and also at a level close but below altSA, to perform emission measurements not impacted

by contrail ice particles. The flight tests should be performed for different cruise thrust settings of the engines of the source aircraft ranging from maximum efficiency to maximum continuous thrust. Conventional fuel should be burned in one engine, blends with alternative fuel in the other. When the focus of the flight test is on aged contrails, best both engines should burn the same fuel and a comparison of contrail properties for different fuels is performed by comparing successive test flights.

Table 6-1 provides recommendations of measurements for the ground and flight tests. Proposed instrumentation for these measurements is provided in Section 7.

Specific forecast products are required for the planning of the flight tests: meteorological forecasts including pressure altitudes where the Schmidt-Appleman criterion for contrail formation is fulfilled, and relative humidity over ice.

Table 6-1: Recommended measurements for emission ground and emission/contrail flight tests.

Aircraft /engines	Position (DGPS) / fuel flow, N1, N2, EGT.
Met. Parameter	P, T, relative humidity
Aerosol	Total particle number and size Non-volatile particle number and size Black carbon number and mass Sulfate, organics fraction and mass Cloud condensation nuclei Particle hygroscopicity
Gaseous species	CO_2, CO SO_2, H_2SO_4 NO, NO_2, HONO, HNO_3, NO_y Hydrocarbons, low-volatile hydrocarbons
Ice crystals	Particle number and size Particle shape

7. Detailed proposals for practical tests

7.1. Engine tests – biofuels and kerosene / biofuels

The emission behaviour of alternative fuels including biofuels can differ from the one of kerosene. Besides comprehensive testing on subscale and subsystem level, full scale engine tests provide the actual emission data and are therefore essential to validate the emission model at engine level. However, since the test setup is more complex and expensive, the measurement time and conditions are limited and hence the test matrix has to be chosen carefully, according to the findings of the aforementioned investigations on subsystem level.

In the last years, several experimental investigations have been performed aiming on the emissions pattern of combustors and turbo engines operated with alternative jet fuels, mostly SPK-fuels (GtL, BtL, CtL), and HEFA. Quite recently, the latest approved alternative fuel component - Farnesane (SIP-fuel) - was also investigated. Studies on emission pattern in exhaust plumes are limited. The fuels were studied both neat and in blends with petroleum-derived fuels [ALFA-BIRD 2007-2013, Altaher et al. 2014, Anderson et al. 2011, Bhagwan et al. 2014, Blakey et al. 2011, Bulzan et al. 2010, burn-FAIR 2011, SWAFEA 2011, Cain et al. 2013, Christie et al. 2012, DeWitt et al. 2008, ECLIF 2015, Li et al. 2013, Lobo et al. 2012, Moore et al. 2015, Moses 2008, Rahmes et al. 2014, Saffaripour et al. 2014, Saffaripour et al. 2011, Snijders et al. 2011, Timko et al., 2015, Wahl et al., 2014, Wahl et al., 2012, Wahl et al. 2011, Zschocke et al. 2015], as a response to the approval protocol.

In these previous investigations, the emissions were shown to depend also on the power setting of the engine and the operating condition (e.g. flight altitude). The power settings most known are those following the LTO-cycle (landing–takeoff, ICAO): Taxi, approach, climb, and take-off, corresponding to 7%, 30%, 85%, and 100% of takeoff thrust. These power settings are seen as a minimum requirement and allow a comparison to the certification information of current aircraft engines within the ICAO emission databank[12]. Engine thrust settings are therefore of importance in gathering the target data, e.g. NO_x levels or soot particles at all relevant operating conditions. Only then, a complete data base can be established, as a prerequisite for a correct prediction of emission and their impact on environmental issues. A comprehensive data base is also essential in order for model validation and transfer of the results to other operating conditions.

In summary, the previous evaluations have shown that the emission pattern of alternative aviation fuels show a different picture compared to the one of Jet A-1: Major gaseous emissions (CO, CO_2, and UHC) were reduced slightly, depending also on thrust; particulate matter (PM) emissions were significantly reduced (both in mass and particle number); considering NO_x, no clear trend is reported, although mostly reported to be reduced. The lack of knowledge on physical properties was seen as a major reason for not be able to interpret the experimental findings in a clear way.

Detailed proposals for practical tests are suggested based on the findings of the aforementioned work packages including experiences from relevant measurement campaigns focusing on emissions of alternative aviation fuels. It is needed to perform measurements, with different kinds of biofuels, neat and blended (50% to kerosene), for major pollutants and combustion products. The emissions to be measured include

[12] Up to date soot particle data are not included in the ICAO certification databank. Instead, the so-called Smoke Number (SN) is reported to represent the tendency to produce soot. However, correlation methods exist to transfer the SN into a particle concentration (see section 5).

gaseous emissions: CO, CO_2, NO_X, UHC, as well as particle emissions including mass, number, and size, as well as aromatics and aldehydes, besides sulphur containing species although not assumed to be present in neat synthetic jet fuels. In addition, ambient conditions (such as humidity and temperature) as well as physical properties such as viscosity or mean Sauter diameter should be part of the studies.

Different types of tests are suggested under real engine operating conditions. On one hand, data are needed for the validation of a particular model; so measurements performed at sea level static conditions will provide the needed information. On the other hand, data must be gathered, under real in-flight conditions. These measurements should be performed at typical cruise flight altitudes and engine conditions, ideally with several engines typical of today's airlines fleet. For reference, experiments with a reference fuel (Jet A-1 or any other certified jet fuel) are highly recommended.

Extensive aircraft engine testing in an engine test bed or under wing measurements including high altitude test rigs are recommended. Compared to under wing measurements, an engine test bed setup would allow for an extension of the operating range of the engine up to full thrust power.

Care has to be laid on an appropriate planning, i.e. on the monitoring of engine performance parameters, and the measurement techniques to be applied under representative operating conditions. All measurements with alternative fuels should be accompanied by measurements with crude-oil based kerosene, of known detailed composition, for reference reasons. Of course, the composition of the alternative fuel to be measured must be determined, too. In addition, knowledge on major physical properties of the fuels of interest must also be provided, due to the interactions between chemistry, fuels performance and turbulence when burning a fuel in a jet engine. Only then, a sound comparison between data stemming from alternative fuels and from Jet A-1 can be done, allowing to interpret the experimental and modeling findings; and to evaluate a possible impact of the emission pattern of a fuel of interest traced back to its chemical composition and physical properties, as well.

Three different types of ground based engine tests are to be performed in order to deliver valuable input. At first, measurements of the emissions of an aircraft's engine operated with alternative fuels. Secondly, if possible, measurements should be performed for a variety of different types of engines. Thus, the performance of (an) alternative (e.g. biomass based) synthetic fuels can be evaluated on a broader, more meaningful basis. In addition, such measurements might be conducted in a high altitude test facility, to account for testing core engine, engine component as well as the entire engine system under flight condition, i.e. temperature, pressure, flow air, and Mach number. Such experiments would allow the measurements of further important variables which will be helpful both for the model development describing the sub-processes and the assessment of the fuels' performance. Thirdly, measurements should be performed at the airfield, to check the possibility of attributing the emissions measured to a specific fuel, and thus, to a specific scheduled flight. This would address efforts how to improve the local air quality at and near the airfield, thus reducing the fuel's impact on the local environment.

7.2. Ground and flight tests

The purpose of the tests is to measure engine emissions (gases and particulates) in static ground conditions and in-flight (near- and far-field) to assess the effect of certified alternative/biofuels fuels and blends on contrail onset and properties relative to Jet A-1 fuel. An important parameter to vary between the different fuels is the content and type of aromatics, i.e. type of hydrocarbon mainly responsible for the formation of soot. Another parameter to vary is the sulphur content in the fuel.

Sulphuric acid formed in the exhaust from the fuel sulphur may play a role in activating the soot in the exhaust to condensation nuclei under threshold conditions for contrail formation.

All fuels used during the tests need to be certified and meet the requirements of both specifications: ASTM D1655 and DEF STAN 91-91. After transported to the field site, the fuels should be analysed again including determination of the content and composition of aromatics. In addition fuel samples should be taken after each flight and ground test from the tanks of the source aircraft, because of residual fuel in the tanks from the former test runs.

The runway, taxiway, pavement, and ground test area of the airfield used as base for the field measurements must be certified for the sample and source aircraft. Ground test instrumentation need to be integrated in containers or vans. All necessary components outside these containers/vans (e.g. inlet probes and lines) need to be secured to the ground/basement of the test facility by means of suitable screwed connection or approved adhesives, to avoid any objects entering the engine during operation. The area around the source aircraft need to be clear of any personnel during the test runs. The engines will be operated with alternative and conventional fuels at different thrust settings, as far as possible according to the ICAO-LTO cycle (this may not be possible for the highest trust levels). The orientation of the source aircraft and the exhaust inlet probes downstream should be in the predominant wind direction. Sampling loss of particles, depending on particle size, in the inlet lines need to be determined by calculations and experimental tests. The environmental conditions (e.g. temperature, wind speed and direction) during the test runs should be registered. In order to avoid growth of particles by condensation, the sample flow needs to be diluted with dry nitrogen supplied by gas bottles. All personnel on site during the test runs must wear ear protection devices.

A safety assessment must be made for the flight tests including near field (50-200 m) and far field (5-10 nmi) sampling of the measurement aircraft in the wake of the source aircraft. This includes considerations of wake vortex strength of the source aircraft and airframe stability of the sampling aircraft as well as operational rules during the formation flight. The sampling aircraft should enter the wake/exhaust trail in the near-field from below and alternate between measurements behind the left and right engine. During the far-field measurements both engines of the source aircraft should burn the same fuel type since emissions of both engines and resulting contrails will be partly mixed already at the far-field distance.

Suitable instruments for the measurements recommended for the ground and flight tests are listed in Table 7-1. Instruments providing on-line measurements are recording data with averaging times of one to a few seconds.

Table 7-1: Gas and particle measurements and instruments for ground and flight tests of jet engine emissions and contrails

Gaseous species		**Particles**	
Parameter	Instrument	Parameter	Instrument
CO_2	NDIR, CRDS	Total aerosol number & size	CPC, OPC, SMPS, OPC, APS, UHSAS
CO	VUV- pulsed fluorescence	Non-volatile aerosol number & size	Thermo denuder & CPC, SMPS, OPC, APS
SO_2, H_2SO_4	CIMS	BC number & mass	SP2, MAAP
NO, NO_2	Chemiluminescence (CL), Photolytic reduction & CL	Sulfate, organic aerosol fraction	AMS, filter
HONO, HNO_3	CIMS	Cloud condensation nuclei	CCN detector
NOy	Au reduction converter & CL	Particle hygroscopicity	SMPS & humidifier
HC	PTRMS	Ice particle number and size	CAS, 2DS
Organic acids	NI-CIMS	Ice particle shape	2DS

8. Conclusions

In this chapter we provide summaries and recommendations distilled from the foregoing chapters.

8.1. Contrail formation from various fuels

Contrail formation is a thermodynamically controlled process that can theoretically be described by the Schmidt-Appleman criterion. This states that contrails form once the expanding plume gets transiently water-supersaturated (i.e. its relative humidity with respect to liquid supercooled water exceeds 100%) during mixing with cold ambient air. The Schmidt-Appleman criterion depends in particular on fuel and engine properties, namely the fuel's emission index of water vapour, EI_{H2O}, the fuel's lower heating value (specific energy content), LHV, and the engines' overall propulsion efficiency, η. The latter depends itself slightly on fuel composition. Alternative fuels currently under examination (drop-in fuels or similar) differ from kerosene in these quantities, yet merely very little (less than 10% of the kerosene values), so that contrail formation is very little affected. We expect that neat alternative fuels lead to contrail formation at a slightly higher (about 0.75°C) ambient temperature than kerosene. As the temperature decreases with altitude in the troposphere with 0.65°C per 100 m, we expect that contrail formation will start at about 100-150 m lower altitudes than today after a transition to neat alternative fuels. For blends with kerosene the expected changes in contrail formation are proportionally smaller.

A transition from kerosene to alternative fuels or blends will affect contrail formation only on cruise levels that are just at the Schmidt-Appleman threshold (the altitude where the temperature is just low enough that the criterion is fulfilled). It is necessary to determine which fraction of flights actually occurs just at this threshold in order to see whether the slight changes in contrail formation are climatically important or not.

8.2. Contrail properties derived from various fuels

Much more important than effects on contrail formation are effects on contrail properties from different fuels. The most important change in this sense is that neat alternative fuels are essentially free from aromatics and sulphur, which both are precursors of particles in the exhaust plume, namely soot particles and volatile sulphuric acid/ water solution droplets. Soot particles in turn are the most important nuclei for water condensation and subsequently of ice crystal (i.e. contrail) formation under current (soot rich, soot emission index exceeding 10^{14} particles per kg fuel) conditions. A few degrees below the Schmidt-Appleman threshold almost all soot particles serve as ice nuclei and lead to an ice crystal, thus the number concentration of ice crystals is strongly controlled by the emission rate (by number) of soot particles. It is expected that an introduction of alternative fuels will lead to a reduction of emission of soot particles, thus essentially to contrails with lower initial ice crystal concentrations than compared to flying with kerosene.

It has also been shown that volatile particles and particles from ambient air start to contribute to ice formation under soot poor conditions (where the soot emission index is lower than 10^{12} to 10^{13} per kg fuel), and that the initial ice crystal concentration can even rise with decreasing soot emission under certain circumstances. Thus, a too strong reduction of soot emissions (say stronger than a factor 1000) can have adverse effects, in particular at high altitudes (low temperatures).

Other adverse effects from a transition to alternative fuels can occur close to the Schmidt-Appleman threshold. The number of ice crystals that are formed increases strongly with the distance from the threshold. As the threshold is lower (in altitude) for alternative fuels than for kerosene, flight at the kerosene threshold with kerosene could produce less ice crystals than a flight at the same altitude with alternative fuels. This is again a threshold problem, and needs further study. The threshold effect will also be modified by the low sulphur level in the exhaust of alternative fuels, which complicates the situation. Whether the effect is an important one can only be determined by a statistical evaluation of how many flights actually occur in proximity to the Schmidt-Appleman threshold and by measurements.

8.3. Climate impact from contrails of various fuels

The initial reduction of crystal number concentration has various important consequences for the climate impact of contrails from alternative fuels and blends. As the ice mass that constitutes a contrail is almost completely provided by the moisture of the ambient air (and not by the emitted water vapour), the fuel type has no effect on the ice mass. Ice crystals are therefore on average larger in a contrail with less ice crystals (as for alternative fuels) and smaller in a contrail with more ice crystals (as for kerosene). As the ice mass is the same, the optical thickness and radiative effects of contrails depend inversely on crystal number concentration, that is, they are smaller for alternative fuels than for kerosene. Furthermore, larger ice crystals (those formed from burning alternative fuels) fall faster through the air than smaller ice crystals (from burning kerosene). Crystal falling (termed sedimentation) is an important microphysical process leading to termination of a contrail. Thus, ceteris paribus, it is expected that contrails from alternative fuels have lower effects on the flow of radiation through the atmosphere and they terminate earlier than their

counterparts from kerosene. Thus, a benefit for climate is generally to be expected from a transition to alternative fuels, but there may be more or less prudent ways to use alternative fuels in the aviation system. To obtain an optimum benefit needs further research.

Investigation of the potentially large beneficial effects is still in its infancy. First results suggest that the climate benefit is not proportional to the initial reduction of ice crystal formation. This would imply that substantial climate benefits can only be expected for substantial replacement of kerosene with alternative fuels. It might be that it is better to use constrained stocks of biofuels in certain geographical regions or in certain seasons where a greater benefit can be achieved than in other regions and seasons. For instance, contrails that are terminated by synoptic forcing (downward motion of the air) have a smaller potential for climate benefit than contrails that terminate because of crystal sedimentation. It would thus be reasonable to use biofuels primarily for flight in regions and seasons where contrails are primarily terminated by sedimentation. It needs further climate studies to find which termination process occurs when and where.

8.4. Fuel's impact on combustion system sub-processes

The formation of emissions, in particular of soot particles, is considered to have the potential of a noticeable impact on climate. The formation of soot particles is resulting from the specific components of the fuel of interest. The complexities in a jet fuel in conjunction with the wide parameter range when burning in a jet engine, under turbulent conditions and at high altitude, are the major challenges in achieving a comprehensive understanding and description of the emission pattern of the fuel of interest.

Potentially each process occurring in a combustion chamber, whether it is related to the fuel placement, to the ignition, to the split between the pilot burner and the main burner, to the staging, to the cooling, to the dilution etc. has an impact on emissions. Moreover a majority (not all) of these sub-processes are fuel composition dependent. It is definitely necessary to investigate the impact of conventional and alternative fuels on existing and future engine architectures and combustion system technologies (e.g. ground and flight measurements). It is also necessary to de-couple these processes and investigate the impact of fuel's composition on individual sub-processes.

The recommendation is here to use existing or to-be-designed specific experiments and rigs to isolate those sub-processes. Then, the proper metrology and diagnostics coupled with research simulation codes can give access to qualitative knowledge and quantitative measurements which allow understanding the true relationship between fuel composition and the sub-process under investigation.

Furthermore, the need of developing validated chemical models is stressed. Such a model will allow studying the effect of the chemical composition of the fuel of interest on the fuel's properties, in particular on the combustion process, i.e. its emissions, and thus, the evaluation of its impact on climate. Thus, it is ensured that the combustion process and the emission pattern can be studied in detail, for a specific question, e.g. effect of a specific aromatic molecule or of other molecules, e.g. cyclic or iso-alkanes on the amount of soot particles, within the whole parameter range. This was identified as a major open question.

Of course, the reaction model has to be validated against the relevant parameters and fuels, with representative molecules for the chemical families an alternative fuel might be composed of, and model fuels mimicking a synthetic fuel, among them. Measurements of ignition delay time, laminar flame speed, and species profiles are the

most important ones to be performed. Temperatures, pressures and fuel-air ratios are the most important parameters identified.

In addition, once a reaction model exists that was validated by measurements covering the whole range of experimental parameters needed, CFD simulations can be used to predict the emission pattern of the fuel of interest under real flight conditions, i.e. taking into account the interactions between fuel placement, fuel combustion, and turbulence mimicking the oxidation of a jet fuel in a jet turbine.

Furthermore, following this strategy, a chemical reaction model will offer a possibility to study the combustion behaviour of future aviation fuels.

In summary, the reaction model can be regarded as a virtual fuel, which can be studied by running CFD simulations, serving as a virtual gas turbine test rig.

8.5. Emission models

Emission prediction models are required to analyse the impact of alternative fuels on engine emissions, particularly in terms of PM. For the quantification of PM emissions, several different models are presented in the literature. These simplified methods aim at a prediction of particle concentration and number, based on a limited parameter set. This approach is appreciated, especially for the application within global air traffic emission inventories, due to the availability of required input data and the reduced computational effort.

It could be shown that former emission models do not account for the potential impact of different fuel types, whereas the current models lack of an appropriate engine performance representation. Therefore it is suggested to focus on both, engine performance and fuel characteristics for the correlation with PM emissions, since the PM emission changes with engine power setting and fuel composition. The PM emission may correlate with characteristic engine parameters, like combustor inlet temperature, pressure and the fuel to air ratio, and with the hydrogen-content or hydrogen-to-carbon ratio to consider fuel aromatic content and aromatic nature. However, it is essential to have a sufficient experimental database of different engine types and alternative fuels to improve the accuracy of the model results and expand the scope of application.

8.6. Ground and flight tests

Experimental data from ground and flight tests are important to improve our understanding of the exhaust composition as a function of fuel composition and the relation of soot emissions and contrail microphysics. The soot formation depends mainly on the content of aromatics in the fuel, however, also on the kind of the aromatics. The latter deserves more in-detail investigations, as it provides the potential to reduce the soot formation without reduction of the present lower limit of aromatics content in the fuel. In addition, the role of further molecules from other chemical families i.e. cyclic and iso-alkanes, need to be addressed, too.

Investigations of the differences in the ice particle size distribution in contrails as a function of the soot emissions are very difficult and corresponding flight data are very sparse. The instrumental uncertainties of the ice particle laser spectrometer probes need to be better quantified and more field experiments on this issue are needed including tests with maximum differences in soot emissions. This may be achieved by using source aircraft with novel low-soot engines burning alternative fuels.

8.7. Short-term mitigation options

The comprehensive introduction of fuels with low soot emission and novel combustion concepts like lean combustion (which produces little soot as well) will take perhaps decades. The most promising mitigation option for the nearer future is thus not a technological one, but an operational one. It is possible to perform flight routing in a more climate-friendly way at a moderate increase in direct operational costs (REACT4C, a European FP7 project, see Grewe et al., 2014). Especially persistent contrails can be avoided when flights are steered clear from ice-supersaturated regions. As these are often only a few 100 m thick, that is, shallower on average than the vertical separation of flight levels, it is possible to avoid them by changing flight altitudes as appropriate. The best results can be achieved when the actual weather (including ice supersaturation) for the flight is predicted and the chemical reactions of the gaseous components and the interaction of these products and of the contrails with atmospheric radiation calculated in advance to the flight. The results of these calculations can be translated into so-called cost functions that can be used in flight planning.

The instantaneous radiation effect of contrails is orders of magnitude larger than the effects of gaseous emissions; it can reach from a strong warming to a strong cooling effect. Thus, it is not necessary to avoid all contrails. It suffices to avoid those that produce the strongest warming. It is of course necessary, that regions and times where contrails will produce strong warming can be predicted reliably. Such methods are in principle available, but still need operational tests and demonstration studies.

List of acronyms

- AAFEX: Alternative Aviation Fuel Experiment
- ACCESS: Alternative Fuel Effects on Contrails and Cruise Emissions
- AFR: Air-to-Fuel Ratio
- ALFA-BIRD: Alternative Fuels and Biofuels for Aircraft Development
- AMS: Aerosol Mass Spectrometer
- APEX: Aircraft Particle Emissions Experiment
- APS: Aerodynamic Particle Sizer
- ATTAS: Advanced Technologies Testing Aircraft System
- BC: Black Carbon
- BTL: Biomass to Liquid
- CAS: Cloud Aerosol Spectrometer
- CCN: Cloud Condensation Nuclei Counter
- CIMS: Chemical-Ionisation Mass Spectrometry
- CL: Chemiluminescence
- CPC: Condensation Particle Counter
- CRDS:Cavity-Ring-Down Spectroscopy
- CTL: Coal to Liquid
- DGPS: Differential Global Positioning System
- 2DS: Stereo Optical Array Cloud Particle Imaging Probe
- ECLIF: Emission and Climate Impact of Alternative Fuels
- EGT: Exhaust Gas Temperature
- EI: Emission Index
- FT: Fischer-Tropsch
- GC: Gas chromatography
- GTL: Gas-to-Liquid
- HACA: Hydrogen abstraction-carbon addition
- HEFA: Hydro-processed esters and fatty acids
- ISSR: Ice-supersaturated region
- LHV: Lower heating Value
- MS: Mass spectrometry
- N1, N2: Speed of low and high pressure compressor
- NDIR: Non-dispersive IR sensor
- MAAP: Multi Angel Absorption Photometer
- OC: Organic Carbon
- OPC: Optical Particle Counter

- PM: Particulate matter
- PTRMS: Proton-Reaction Mass Spectrometry
- RF: Radiative forcing
- SMPS: Scanning Particle Mobility Sizer
- SN: Smoke Number
- SP2: Single particle Soot Photometer
- SPK: Synthetic Paraffinic Kerosene
- SWAFEA: Sustainable Way for Alternative Fuels and Energy for Aviation
- TC: Total Carbon
- UHSAS: Ultra-High Sensitivity Aerosol Spectrometer

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